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> "Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." Just. Lips. *Polit.* lib. i. cap. 1. Not.

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"Meditationis est perscrutari occulta; contemplationis est admirari perspicua .... Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

——"Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condat,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cœlo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu."

J. B. Pinelli ad Mazonium.

ALERE FLAMMAM.

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ERRATUM.

Page 168, line 23 from top, *insert* 15°.

ERRATA IN VOLUME XXXVIII.

Page 232, line 5 from bottom, *for* no electrification *read* comparatively little electrification.
„ 234, „ 10 from top, *for* 6×10^{-5} *read* 6×10^{-11}; *and for* 4·8 per cent. *read* $4{\cdot}8\times10^{-8}$.
„ „ Delete first paragraph of § 14.
„ „ line 11 from bottom, *for* Even *read* But.
„ „ „ 9 from bottom, *for* sufficient *read* insufficient.

THE
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[FIFTH SERIES.]

JANUARY 1895.

I. *Further Studies on Molecular Force.*

By WILLIAM SUTHERLAND*.

IN two recent papers on the Attraction of Unlike Molecules the result has been established, that if two molecules of mass m_1 attract one another with a force $3_1A_1 m_1^2/r^4$, and two of mass m_2 with a force $3_2A_2 m_2^2/r^4$, then an m_1 attracts an m_2 with a force $3({}_1A_1\, {}_2A_2)^{\frac{1}{2}} m_1 m_2/r^4$; from which it follows that Am^2 is resolvable into two factors $A^{\frac{1}{2}}m$ each belonging to a molecule. Now in the "Laws of Molecular Force" (Phil. Mag. xxxv., March 1893), values of M^2l, which is proportional to Am^2, are given for a large number of substances as determined by five methods, so that it is only necessary to take the square roots of the tabulated values of M^2l to get relative values of $A^{\frac{1}{2}}m$. Indeed, in originally studying the values of M^2l, the first step I took was to examine the values of $(M^2l)^{\frac{1}{2}}$; and I noticed the reign of law amongst them, but apparently not over so wide a range of values as was dominated by the empirical law $M^2l = 6S + {\cdot}66S^2$, where S is the sum of certain constants characteristic of the atoms in the molecule, and called the Dynic Equivalents of the atoms. Accordingly this empirical expression was adopted in the "Laws of Molecular Force." Yet even this expression failed to apply to the simpler typical compounds; but in connexion with the values of $(M^2l)^{\frac{1}{2}}$ I have discovered that there are two principles in operation amongst them, one applying to the serial compounds of carbon, and the other to the simpler compounds such as those of inorganic chemistry. The advantage of the empirical expression $M^2l = 6S + \cdot 66 S^2$ was that it happened to lend itself to some of the transition cases which occur between the two classes. But now it is clearly our duty to set aside the empirical law, and confine our attention to $(M^2l)^{\frac{1}{2}}$ proportional to $A^{\frac{1}{2}}m$. The following is a brief statement of the order in which these further studies will be taken, and of their results.

---

* Communicated by the Author.

1. Values of $(M^2l)^{\frac{1}{2}}$ in the carbon compounds, with determination of the parts contributed to them by various atoms and radicals, and proof that in the non-metallic atoms these parts are approximately proportional to the volumes of the atoms.

2. (*a*) and (*b*). Development of two methods of determining $(M^2l)^{\frac{1}{2}}$ for inorganic compounds, especially compounds of the metals, tabulation of the results of the methods, with proof that valency controls the magnitude of molecular force in these compounds. (For example, if RS_n is a compound of a metal R of valency n with n atoms of S, then $(M^2l)^{\frac{1}{2}}$ for RS_n is the sum of a value for R and n times a value for S, all divided by the square root of n.)

3. Determination of $(M^2l)^{\frac{1}{2}}$ for the uncombined metals, with proof that in the main chemical families $(M^2l)^{\frac{1}{2}}$ for each atom is proportional to the square root of the volume of the atom and also to the square root of its valency. Relation between the volumes of the metallic atoms in combination and the parts contributed by them to $(M^2l)^{\frac{1}{2}}$ in their compounds.

4. General summary of results, and analysis of molecular attraction into the sum of atomic attractions, with general statement of their laws.

1. *Values of* $(M^2l)^{\frac{1}{2}}$ *in the Carbon Compounds.*

To begin with, the law of the Dynic Equivalents remains unchanged, for the dynic equivalent of an atom being the number of CH_2 groups which would contribute as much to the value of M^2l for a molecule as the atom does, it remains the same for $(M^2l)^{\frac{1}{2}}$ as for M^2l. This will appear in all the values of $(M^2l)^{\frac{1}{2}}$ that follow. From Table XXV. of the Laws of Molecular Force we get the following values of $(M^2l)^{\frac{1}{2}} \propto A^{\frac{1}{2}}m$ for the paraffins:—

C_3H_8.	C_6H_{14}.	C_8H_{18}.	$C_{10}H_{22}$.
3·8	7·7	9·5	11·2

The difference for each CH_2 group is ·97 from C_2H_6 to C_6H_{14}, ·90 from C_6H_{14} to C_8H_{18}, and ·85 from C_8H_{18} to $C_{10}H_{22}$. There appears to be a progressive diminution in these differences for CH_2. It will be of advantage, therefore, to study a more extended series, such as is given on page 266 of the "Laws of Molecular Force" for the paraffins from C_5H_{12} to $C_{16}H_{34}$, the values of M^2l being got, as there explained, from Bartoli and Stracciati's surface-tensions at 11° C. To complete the series we can obtain approximate values of M^2l for C_3H_8 and C_4H_{10} by the approximate relation $Ml = 1190 v_1 T_b$, given on page 247 of the "Laws of Molecular Force," dividing by 10^6 to reduce to the same units as are employed in table xxv. T_b is the boiling-point measured from absolute zero, and v_1 is the volume of a gramme at the boiling-point: for C_3H_8, $T_b = 246$ and $v_1 = 1{\cdot}75$; and for C_4H_{10}, $T_b = 274$ and $v_1 = 1{\cdot}71$; and thus the values of M^2l to go along with the rest are 22·1 and 32·3; and for $(M^2l)^{\frac{1}{3}}$ we have the series of values and differences:—

TABLE I.

	C_2H_6.		C_3H_8.		C_4H_{10}.		C_5H_{12}.		C_6H_{14}.		C_7H_{16}.		C_8H_{18}		C_9H_{20}.
$(M^2l)^{\frac{1}{3}}$ ……	3·8	|	4·7	|	5·7	|	6·9	|	7·6	|	8·8	|	9·5	|	10·5
Diff. ………		·9		1·0		1·2		·7		1·2		·7		1·0	

		$C_{10}H_{22}$.		$C_{11}H_{24}$.		$C_{12}H_{26}$.		$C_{13}H_{28}$.		$C_{14}H_{30}$.		$C_{15}H_{32}$.		$C_{16}H_{34}$.
$(M^2l)^{\frac{1}{3}}$……	|	11·3	|	12·1	|	13·1	|	13·8	|	14·7	|	15·2	|	100
Diff.… –	·8		·8		1·0		·7		·9		·5		·8	

Here, although the values of the differences for CH_2 are unsteady (doubtless on account of the difficulty of preparing the paraffins pure), there is on the whole a progressive diminution in the value of the difference: thus from C_2H_6 to C_8H_{18} the difference is 5·7, and from C_8H_{18} to $C_{14}H_{30}$ it is 5·2 But in the case of the esters from $C_3H_6O_2$ to $C_{10}H_{20}O_2$, to which we proceed, there is no such diminution. The following are the mean values of $(M^2l)^{\frac{1}{3}}$ for the different isomers under each formula:—

TABLE II.

	$C_3H_6O_2$.		$C_4H_8O_2$.		$C_5H_{10}O_2$.		$C_6H_{12}O_2$.		$C_7H_{14}O_2$.		$C_8H_{16}O_2$.
$(M^2l)^{\frac{1}{3}}$ ……	5·8	|	6·7	|	7·6	|	8·4	|	9·3	|	10·2
Diff. ………		·9		·9		·8		·9		·9	

		$C_9H_{18}O_2$.		$C_{10}H_{20}O_2$.
$(M^2l)^{\frac{1}{3}}$ ……	|	11·3	|	12·1
Diff. .. ……	1·1		·8	

The mean difference is here ·9, which is the mean difference for the paraffin series from C_2H_6 to $C_{14}H_{30}$. The data for other series are as follows :—

TABLE III.

Benzene series ...	C_6H_6. 6·6	C_7H_8. 7·5	C_8H_{10}. 8·4	C_9H_{12}. 9·3	$C_{10}H_{14}$. 10·1
Alkyl iodides	CH_3I. 5·1	C_2H_5I. 6·2	C_3H_7I. 7·1	C_4H_9I. 7·9	$C_5H_{11}I$. 8·9
Alkyl bromides		C_2H_5Br. 5·4	C_3H_7Br. 6·4	C_4H_9Br. 7·3	$C_5H_{11}Br$. 8·1
Alkyl chlorides ... (Fourth method)	CH_3Cl. 4·1	C_2H_5Cl. 5·1	C_3H_7Cl. 5·7		
(Fifth method)			C_3H_7Cl. 6·0	C_4H_9Cl. 7·2	$C_5H_{11}Cl$. 8·1
Alkyl oxides	$(CH_3)_2O$. 4·5	$CH_3OC_2H_5$. 5·5	$(C_2H_5)_2O$. 6·3	$C_2H_5OC_3H_7$. 7·2	$CH_3OC_5H_{11}$. 8·2
Alkyl amines ...... (Fourth method)	NH_5C. 4·2	NH_7C_2. 4·7	NH_9C_3. 5·7	$NH_{11}C_4$. 6·4	$NH_{15}C_6$. 8·1
(Fifth method) ...	$NH_{11}C_4$. 6·1	$NH_{13}C_5$. 7·1	$NH_{15}C_6$. 8·0		

These data for these families and for a few other short series, derivable like the above from table xxv. of the "Laws of Molecular Force," can be represented according to the following scheme, wherein the meaning of the column headed $M\beta$ will be explained in a little.

TABLE IV.

Substance.	Composition.	$(M^2l)^{\frac{1}{2}}$.	$M\beta$.
Paraffin	$H+ H+nCH_2$	$2·2+·9n$	$9 +15·7n$
Chloride	$Cl+ H+nCH_2$	$3·3+·9n$	$23·5+16n$
Bromide...............	$Br+ H+nCH_2$	$3·6+·9n$	$29 +17n$
Iodide	$I+ H+nCH_2$	$4·3+·9n$	$36 +16·4n$
Oxide	$O+2H+nCH_2$	$2·7+·9n$	$14 +17·3n$
Amine	$N+3H+nCH_2$	$3·1+·9n$	$20 +17·3n$
Ester	$COO+2H+(n-1)CH_2$	$4·0+·9(n-1)$	$29 +17·5(n-1)$
Benzene series	$C_6H_6+nCH_2$	$6·6+·9n$	$75·5+16·8n$
Cyanide (nitrile) ...	$CN+ H+nCH_2$	$3·5+·9n$	$24 +17n$
Sulphide	$S+2H+nCH_2$	$3·8+·9n$	$26 +17n$
Nitro-compound ...	$NO_2+H+nCH_2$	$3·9+·9n$	$29 +17n$
Nitrate	$NO_3+H+nCH_2$	$4·3+·9n$	$36 +17n$
Sulphocyanate	$CNS+H+nCH_2$	$4·9+·9n$	$41·5+17n$

This scheme embodies the principle of the Dynic Equivalents, for an atom such as I is represented as producing the same effect on the value of $(M^2l)^{\frac{1}{2}}$ whatever may be the number of CH_2 groups it is associated with. In the "Laws of Molecular Force" it was shown that there is a striking parallelism between the values of the dynic equivalents of the atoms and of their refraction equivalents. I had a strong impression that this must be due to the fact that both quantities were nearly proportional to the volumes of the atoms, but was not then able to test the idea through lack of values of the volumes of the atoms. But by means of the characteristic equation for liquids given in that paper, and an unpublished simplified form of it, I have been able to get approximate values of the limiting volumes of the members of a number of series of compounds. Let β be the limiting volume of a gramme of substance of molecular mass (weight) M; then the differences in $M\beta$ for a difference CH_2 in composition are as follows:—paraffins 15·7, alkyl iodides 16·4, alkyl bromides 17, alkyl chlorides 16, alkyl oxides 17·3, alkyl amines 17·3, esters 17·5, and benzene series 16·8. The values of $M\beta$ for the lowest available members of these series are CH_4 25, CH_3I 52, CH_3Br 46, C_2H_5Cl 55·5, $(C_2H_5)_2O$ 83, NH_3 20, $C_3H_6O_2$ 64, and C_6H_6 75·5; so that for $M\beta$ we have the schemo given above with $(M^2l)^{\frac{1}{2}}$.

The following are the few data on which the numbers in the scheme for the nitriles, sulphides, nitro-compounds, nitrates, and sulphocyanates are founded, on the assumption that in $(M^2l)^{\frac{1}{2}}$ CH_2 has a value ·9 and in $M\beta$ approximately 17.

Table V.

	C_3H_7ON.	$(C_2H_5)_2S$.	CH_3NO_2.	$C_2H_5NO_3$.	CH_3CNS.	C_2H_5CNS.
$(M^2l)^{\frac{1}{2}}$......	6·2	7·4	4·8	6·1	5·8	6·6
$M\beta$.........	75	94	46	70	59	75

In Table IV. there are no values given for the olefine series C_nH_{2n}; but the data for the olefines in table xxv. of the "Laws of Molecular Force" show that $(M^2l)^{\frac{1}{2}}$ for C_nH_{2n} is practically identical with that for C_nH_{2n+2}. On this account the dynic equivalent of the two terminal hydrogens of a paraffin C_nH_{2n+2} was, in the "Laws of Molecular Force," said to be negligible; but the better mode of expression in accordance with the usages of physical chemistry would be to say that the double-bonded union of two carbon atoms in an olefine changes the dynic equivalent of the two carbon atoms by an amount equal to that of the two terminal hydrogen atoms of the paraffin. The first point to be noticed about the expressions for $(M^2l)^{\frac{1}{2}}$ in Table IV. is that in the paraffins the two terminal hydrogen atoms H+H are apparently represented by an initial term 2·2, which is more than twice as large as the value ·9 for CH_2; while in the $M\beta$ expression for the paraffins the term 9 which represents the volume of H+H is only about half of the 15·7 for CH_2. Associated with this peculiarity of the paraffins, there must be taken another, namely, that methane, CH_4, while chemically the first of the paraffins, separates itself absolutely from the series as regards molecular force, but not as regards $M\beta$. In respect of molecular force it behaves as an element, as is shown in the "Laws of Molecular Force," and in the "Viscosity of Gases and Molecular Force" (Phil. Mag. Dec. 1893); and its value of $(M^2l)^{\frac{1}{2}}$, namely 1·5, is only a half of the 3·1 which it would be if it came within the scheme for the paraffins in Table IV. Thus it appears to be necessary for at least two CH_2 groups to be associated before each takes its characteristic value in $(M^2l)^{\frac{1}{2}}$; and this must be connected with the series-building power of carbon. It should be noticed that the value of CH_2 in $(M^2l)^{\frac{1}{2}}$ depends only slightly on the mode of association of the carbon and hydrogen atoms according to the usual structural formulas, because isomeric substances have almost always nearly equal values; thus, according to the equation $Ml = 1190 \times 10^{-6} v_1 T_b$, as v_1 varies very slightly from one isomer to another, we see that amongst isomers $(M^2l)^{\frac{1}{2}}$ varies nearly as the square root of the boiling-point. Take pentane, C_5H_{12}, as an instance: for normal pentane, $CH_3(CH_2)_3CH_3$, the boiling-point is 38° C., while for tetramethylmethane, $C(CH_3)_4$, it is 9°·5 C.; so that $(M^2l)^{\frac{1}{2}}$ for the latter is $(282·5/311)^{\frac{1}{2}}$, or ·953 times that for the former, which, according to the scheme, is 6·7; and, accordingly, there is only a difference of ·3, corresponding to the great difference in structure attributed to these two pentanes. Thus it is not the position of the two terminal H atoms in the paraffins that determines their apparent large value of 2·2; and provisionally we have to recognize two values for H+H, one being 2·2, and the other a fraction of ·9, and must leave the hydrogen atom to be returned to after we have considered some others.

In the alkyl haloid compounds we must regard the halogen atom as displacing one of these terminal H atoms, for the value of each CH_2 group in $(M^2l)^{\frac{1}{2}}$ still remains the same. Hence if we assume that the one terminal H left has a value 1·1 in $(M^2l)^{\frac{1}{2}}$ and 4·5 in $M\beta$, we can calculate at once from the schemes in Table IV. the values of the halogen atoms in

$(M^2l)^{\frac{1}{2}}$, and also the limiting volumes of the atoms, and similarly with the other atoms and radicals involved in Table IV.: for instance, in that Table Cl + H has a value 3·3, whence that of Cl is 2·2; so in $M\beta$ the volume of Cl + H is 23·5, so that the volume of Cl is 19. In this way have been derived from Table IV. the values now given in Table VI. for the parts contributed to $(M^2l)^{\frac{1}{2}}$ and $M\beta$ by various atoms and radicals, which after this will sometimes be denoted by the symbols F and B: in the third row of numbers are given the values of the ratio B/F.

TABLE VI.

	Cl.	Br.	I.	O.	COO.	S.	NO_2.
B............	19	24·5	31·5	5	20	17	24·5
F............	2·2	2·5	3·2	·5	1·8	1·6	2·8
B/F	9	10	10	10	11	10	9

	NO_3.	CN.	CNS.	CH_2.	C_6H_6.	NH_2.	H.
B............	32	19·5	37	17	75·5	20	4·5
F............	3·2	2·4	3·8	·9	6·6	3·1	1·1
B/F	10	8	10	19	12	6·5	4

For the first ten atoms and radicals the approach in the ratio to constancy is close enough to show that F is nearly proportional to B, or that attracting-power in these atoms is nearly proportional to the volume of the atom; the mean value of the ratio for the first ten is 10, of which the value for CH_2 is nearly double, and that for the terminal H of paraffins less than half; the value for NH_2 will be considered presently along with those of some other compounds of hydrogen. It would appear from the values for NO_2, NO_3, CN, and CNS, that the value for N of F is 1·7, and of B is about 15.

It will be useful at this stage to consider the values of $(M^2l)^{\frac{1}{2}}$ and $M\beta$ in those inorganic compounds for which they are obtainable from table xxv. of the "Laws of Molecular Force."

TABLE VII.

	CO_2.	CS_2.	SO_2.	N_2O.	C_2N_2.	HCl.	H_2S.
$M\beta$............	30	50	35	29	38	27	24
$(M^2l)^{\frac{1}{2}}$	2·7	5·2	3·9	3·0	4·2	2·7	3·2
Ratio	11	10	9	10	9	10	7

	H_2O.	NH_3.	PCl_3.	$AsCl_3$.	$POCl_3$.	$PSCl_3$.	POC_2H_5Cl.
$M\beta$............	14	21	72	73	80	92	78
$(M^2l)^{\frac{1}{2}}$	2·4	2·9	6·6	7·0	7·6	8·4	7·9
Ratio	6	7	11	10	11	11	10

	$CHCl_3$.	CCl_4.	CCl_3NO_2.	C_2Cl_4.	$SiCl_4$.	$SnCl_4$.
$M\beta$............	72	80	86	87	92	101
$(M^2l)^{\frac{1}{2}}$	6·1	6·8	7·6	8·1	6·9	7·8
Ratio.........	12	12	11	11	13	13

For the first six compounds the ratio is the same as the average in the last Table; but in H_2S, H_2O, and NH_3 it falls to a lower value, the reason for which appears to be the presence of the H atoms operating like the two terminal H atoms in the paraffins. To see whether this is the case, let us suppose S, O, and N carry the values already found for them into $(M^2l)^{\frac{1}{3}}$ and $M\beta$, then we get for

	H_2 in H_2S.	H_2 in H_2O.	H_3 in NH_3.
B	7	9	6
F	1·6	1·9	1·2
B/F	4·4	4·7	5·0

In each case the ratio comes near to the value 4 found for the terminal H in the paraffins; though both in $(M^2l)^{\frac{1}{3}}$ and $M\beta$, H_3 in NH_3 appears smaller than H_2 in H_2S, H_2O, or the paraffins.

Returning to the values of the ratio in Table VII., the values for the compounds of P and As seem also to come near to the value 10; but this has no particular significance, as we shall see later on that a different principle is at work amongst some of these compounds; even at present we can see that $(M^2l)^{\frac{1}{3}}$ for PCl_3 has a value 6·6, which is exactly three times the value adopted for Cl, leaving nothing for P; and when we turn to the value for CCl_4, namely 6·8, which is a good deal less than that for 4Cl, we must recognize clearly that we are getting into a type of compound in which the pure additive principle ruling in the carbon series no longer applies. Of course, in connexion with CCl_4 it may be said that it might be expected to be exceptional because CH_4 is so; but then CH_3Cl and CH_3I are not exceptional, a fact well worthy of attention in view of the exceptional nature of CH_4. Indeed, if we take the series of ratios 9 for Cl, 12 for $CHCl_3$, and 12 for CCl_4, with 13 for $SiCl_4$, and 13 for $SnCl_4$, we see an increasing departure from proportionality between $(M^2l)^{\frac{1}{3}}$ and volume $M\beta$, which will become comprehensible when we have dealt with inorganic compounds as a whole. An attempt to trace the intermediate cases, such as that of $CHCl_3$, would lead us into too much detail, though promising light on the great old controversy in chemistry between the dualistic and unitary theorists and on the transition from electrolyte to non-electrolyte.

But without going into transition cases, there are a few more values which we ought to discuss before leaving the carbon serial compounds, as they bear upon the large value of F which belongs to the H atom when apart from the radicals CH_2 and NH_3. The values of $(M^2l)^{\frac{1}{3}}$ for benzene and its monohalogen substitution compounds are :—

C_6H_6.	C_6H_5Cl.	C_6H_5Br.	C_6H_5I.
6·6	7·6	8·2	9·0

which give for Cl—H the value 1·0, for Br—H 1·6, and for I—H 2·4; and these, with the values found for the halogens, give for H in benzene the values 1·2, ·9, and ·8, the mean of which is 1·0; still a large value and nearly equal to the 1·1 belonging to each CH in benzene, which, it should be noticed, is larger than the ·9 for CH_2. Strictly speaking, all that the last numbers really show is that the difference between the halogens and hydrogen in benzene is about the same as the difference between the halogens and the terminal hydrogen in paraffins. The following values form the beginning of a series which, if extended, would illustrate the transition from one type to the other:—

	C_2H_6.	C_2H_5Cl.	$C_2H_4Cl_2$.	$C_2H_3Cl_3$.
$(M^2l)^{\frac{1}{3}}$	4·0	5·1	6·7	7·6

They give Cl—H = 1·1, 2(Cl—H) = 2·7, and 3(Cl—H) = 3·6, which are in fair enough agreement. In the following cases we have only CH_2 groups and halogens.

	$C_2H_4Cl_2$.	$C_3H_6Cl_4$.	$C_2H_4Br_2$.	$C_3H_6Br_2$.
$M\beta$	68	......	76	91
$(M^2l)^{\frac{1}{3}}$	6·7	7·5	7·1	7·8

With ·9 for CH_2 in $(M^2l)^{\frac{1}{3}}$, these give for Cl the values 2·45 and 2·4, and for Br 2·65 and 2·55, which are a little larger than those adopted from the series, namely 2·2 and 2·5.

The data of table xxv. of the "Laws of Molecular Force" furnish values of $(M^2l)^{\frac{1}{3}}$ for the elements H_2, O_2, and N_2, and for CH_4, which are gathered into

TABLE VIII.

	H_2.	O_2.	N_2.	CH_4.
$M\beta$..................	8·6	19·3	22·7	25
$(M^2l)^{\frac{1}{3}}$	·47	1·08	1·11	1·5
Ratio	18	18	20	17

To these may be added an uncertain set of values for Cl_2, namely $M\beta = 34$ and $(M^2l)^{\frac{1}{3}} = 2·4$, their ratio being 14; excepting this, we see that the element gases and CH_4 have nearly a constant value 18 for the ratio $M\beta/(M^2l)^{\frac{1}{3}}$, a value which is nearly double the 10 for atoms in the combined state. It should be noticed that the ratio 19 for CH_2 in the carbon series ranges itself along with the values for the elements and CH_4. It is very remarkable that as regards molecular force, CH_4 not only detaches itself so completely from the paraffins and compounds in general, but also attaches itself so consistently to the elements. It is interesting to find C_2H_4, which is the first of the olefines, detach itself from its class; in the "Laws of Molecular Force" it was proved to have a characteristic equation intermediate in form to those for elements and compounds. It has already been pointed out that the olefine C_nH_{2n} has the same value of $(M^2l)^{\frac{1}{2}}$ as the paraffin C_nH_{2n+2}; but this does not apply to C_2H_4, because instead of the 4·0 for C_2H_6, it has the value 2·5 for $(M^2l)^{\frac{1}{2}}$, and for $M\beta$ it has 43, which is much larger than the 34 of two ordinary CH_2 groups; the ratio $M\beta/(M^2l)^{\frac{1}{2}}$ is 17, which goes with the values found for CH_2 and CH_4.

The case of the elements will be returned to when the methods of getting further data have been developed in the following parts of this paper.

To close for the present the discussion of the carbon serial compounds, the main result had better be restated, as it has perhaps been obscured by foreign details; it is embodied briefly in Table IV., and is this, that the attracting-power of a molecule is the sum of powers belonging to its atoms, the power of an atom varying with its chemical function, but remaining constant when that function is constant. As a subsidiary result, it has been shown that the attracting-powers of the atoms of Cl, Br, I, O, S, N, and C (C unattached to H) are approximately proportional to their volumes in the combined state.

2. (*a*) *and* (*b*). *Methods of finding* M^2l *for Compounds of the Metals, with Results.*

(*a*) While we are on the present line of investigation, it will be convenient to consider such values (relative) of the parameter of molecular force, that is of $(M^2l)^{\frac{1}{2}}$, as are obtainable for solids, both element and compound. These can be got in two ways: first, from the surface-tension of the solids at their melting-points, which are still measurements made on liquids, but at the transition-point into solidity; and second, from the principles of "A Kinetic Theory of Solids" (Phil. Mag. vol. xxxii.). According to the "Laws of Molecular Force" (Phil. Mag. March 1893, p. 258), l in terms of the 10^6 dynes as unit of force is given by

$$l=2\times 5930\alpha v^{\frac{4}{3}}M^{\frac{4}{3}},$$

where α is the surface-tension in grammes weight per metre at ⅔ of the absolute critical temperature, which is near the ordinary boiling-point, v is the volume of unit mass at the same temperature, and M the ordinary molecular mass (weight); so that with the megamegadyne (10^{12} dynes) as the unit of force, we have

$$M^2l = 2 \times 5930 \times 10^{-6} \alpha (M/\rho)^{\frac{4}{3}}. \quad . \quad . \quad . \quad (1)$$

In the case of melted solids α has been measured at the melting-point only; and as the absolute melting-point of solids is not a constant fraction of their absolute boiling-points, we shall have to be content with comparatively rough approximations to the values of M^2l, if in the above equation (1) we use the value of α at the melting-point instead of that at ⅔ of the critical temperature. In the case of mercury the surface-tension at the melting-point has been found by Quincke to be 58·8 grammes weight per metre; and I have estimated that at the boiling-point, if mercury behaves as an ordinary liquid, the surface-tension would be 42·6. Then, to keep the values of M^2l in a rough way more comparable with those hitherto discussed, we will for all the melted solids take α at ⅔ of the critical temperature as roughly given by 42·6/58·8 times its value at the melting-point; denoting which by α_m, we have, when we likewise allow for the difference between ρ at the melting-point and at ⅔ of the critical temperature by a factor 1·09, the equation

$$\begin{aligned} M^2l &= 2 \times 5930 \times 10^{-6} \times \cdot 723 \times 1\cdot 09 \alpha_m (M/\rho)^{\frac{4}{3}} \\ &= 9346 \times 10^{-6} \alpha_m (M/\rho)^{\frac{4}{3}}. \quad . \quad . \quad . \quad (2) \end{aligned}$$

To preserve continuity in the work this equation will be applied first to compounds only, and later on to the metals. It is to Quincke that we owe the first measurements of the surface-tensions of a number of elements and compounds at their melting-points (Pogg. *Ann.* cxxxv. & cxxxviii.); and there are some more recent measurements for a number of compounds by Traube (*Ber. der Deut. chem. Ges.* xxiv. p. 3074). The values of the surface-tension given by Quincke in his second paper are brought into better agreement with those of his first and with Traube's when multiplied by 1·4, and accordingly these values multiplied by 1·4 are entered in brackets in the following Table as values of α_m, and the numbers derived from them are put in brackets also. The density at 15° C. will be used in place of that at the melting-point, because too few values at the melting-point are known, and the difference between the two is really immaterial in comparison with other unavoidable roughnesses in these calculations. The formula by which Quincke calculated α_m from his experimental data is not exact (see Worthington, Proc. Roy. Soc. xxxii.); but his values have been taken as exact enough for present purposes. The first set of data for all the K and Na compounds are Traube's, the rest are Quincke's.

TABLE IX.

Compounds of Potassium.

	KF.	KCl.			KBr.		KI.	
α_m	14·2	10·0	9·5	(10·0)	9·3	(6·9)	8·5	(8·4)
ρ	2·45	1·98	...	...	2·69	...	3·08	
$(M^2l)^{\frac{1}{3}}$ ...	5·1	6·3	6·1	(6·2)	6·9	(6·0)	7·8	(7·8)
M/ρ	23·7	37·6	...	...	44·2	...	53·8	

	KNO_3.			KNO_2.	$KClO_3$.	$KBrO_3$.
α_m	10·0	10·0	(10·0)	10·9	8·8	9·5
ρ	2·07	...	...	2·00	2·32	3·27
$(M^2l)^{\frac{1}{3}}$	7·8	7·8	(7·8)	7·3	7·8	7·9
M/ρ	48·8	...	...	43·0	52·8	51·2

	KCN.	KCNO.	K_2CO_3.			K_2SO_4.		
α_m	9·8	11·9	16·7	16·3	14·8	...	18·1	16·7
ρ	1·52	2·05	2·26	...	...	2·66	...	...
$(M^2l)^{\frac{1}{3}}$	6·9	7·1	12·1	12·0	11·4	...	13·4	12·8
M/ρ ...	42·8	39·4	61·1	...	...	65·3	...	...

	$K_2P_2O_6$.	K_2CrO_4.	$K_2Cr_2O_7$.	$K_2Cr_3O_{10}$.
α_m	14·0	13·5	13·5	13·1
ρ	2·26	2·68	2·67	2·65
$(M^2l)^{\frac{1}{3}}$	17·4	12·6	17·8	22·6
M/ρ	104·4	72·4	111·0	149·3

Compounds of Sodium.

	NaCl.			NaBr.		$NaNO_3$.		$NaNO_2$.
α_m	11·6	11·6	(9·5)	10·5	(7·0)	11·6	(11·2)	12·2
ρ	2·15	...	...	3·0	...	2·18	...	2·10
$(M^2l)^{\frac{1}{3}}$ ...	5·2	5·2	(4·7)	6·0	(4·9)	6·9	(6·8)	6·2
M/ρ	27·2	...	...	34·4	...	39·0	...	33·0

	NaCN.	$NaClO_3$.	Na_2CO_3.			Na_2SO_4.		
α_m	10·9	9·4	21·0	18·2	16·6	18·4	18·5	18·6
ρ	1·50	2·47	2·46	...	...	2·68	...	...
$(M^2l)^{\frac{1}{3}}$ ...	5·8	6·7	10·2	9·5	9·1	11·3	11·4	11·4
M/ρ	33	43	43	...	...	53	...	...

Table IX.—Compounds of Sodium (*continued*).

	Na_2CrO_4.	$Na_2Cr_2O_7$.	$Na_2B_4O_7$.	Na_2WO_4.	$Na_2P_2O_6$.	$Na_4P_2O_7$.
α_m	18·6	14·8	17·8	19·7	17·3	24·7
ρ	...	2·90	2·37	5·50	2·48	2·53
$(M^2l)^{\frac{1}{2}}$ ...	11·2	15·9	16·5	12·5	15·8	23·2
M/ρ	52	91	85	57	82	105

Other Compounds.

	LiCl.		Li_2CO_3.	AgCl.		AgBr.
α_m	12·1	(9·0)	15·5	19·0	(30·3)	17·3
ρ	2·00	...	2·11	5·55	...	6·42
$(M^2l)^{\frac{1}{2}}$	4·3	(3·7)	7·4	6·3	(8·0)	6·7
M/ρ	21·2	...	35·1	25·8	...	29·3

	$CaCl_2$.		$SrCl_2$.	$BaCl_2$.
α_m..................	15·3	(14·1)	(15·3)	(21·4)
ρ	2·22	...	2·96)	3·85
$(M^2l)^{\frac{1}{2}}$	9·8	(9·5)	(10·6)	(12·4)
M/ρ	50·5	...	53·5	54·1

The first point to attend to in these numbers is to ascertain whether the additive principle applies to the values of $(M^2l)^{\frac{1}{2}}$. The differences for K and Na are 1·2 in the chlorides, ·9 in the bromides, 1·2 in the nitrates, 1·1 in the nitrites, 1·1 in the chlorates, 1·1 in the cyanides, of which the mean is 1·1. This is encouraging enough if we remember the roughnesses of calculation and experiment. Proceeding to take the differences for the compounds of the dibasic acids, we get for K_2-Na_2 1·9 in the carbonates, 1·8 in the sulphates, 1·4 in the chromates, 1·9 in the bichromates, and 1·6 in the metaphosphates, the mean of which is 1·72, which is less than twice the mean 1·1 for $K-Na$. It will be shown later that in a compound RS_n, where for instance R represents an n-basic acid and S a monad metal, $(M^2l)^{\frac{1}{2}}=(F_r+nF_s)/n^{\frac{1}{2}}$, where F_r and F_s are the parts due to R and S : according to this principle the value of K_2-Na_2 in the above compounds ought to be only $2^{\frac{1}{2}}$ or 1·41 times the value for $K+Na_1$; while according to the mean values found above, K_2-Na_2 is 1·6 times $K-Na$. In view of the relation for RS_n,

$$(M^2l)^{\frac{1}{2}}/n^{\frac{1}{2}}=F_r/n+F_s,$$

the best plan is to take values of $(M^2l)^{\frac{1}{2}}/n^{\frac{1}{2}}$ which are the sums of F_r/n and F_s or the sum of parts not due to atoms but to equivalents. In the case of the K and Na compounds of the dibasic acids in Table IX., we will reduce the value of $(M^2l)^{\frac{1}{3}}$ to that for equivalents not by dividing by the theoretical $2^{\frac{1}{3}}$ but by the empirical 1·6: for convenience the value of $(M^2l)^{\frac{1}{3}}$ thus reduced to the value for equivalents will be denoted by ΣF_e, the relation between the two being as a rule

$$\Sigma F_e = (M^2l)^{\frac{1}{3}}/n^{\frac{1}{3}},$$

though in the present case we are taking 1·6 in place of $2^{\frac{1}{3}}$ in order to allow for a slight difference in equation (2) as applied to the compounds of the dibasic acids; so also in $Na_4P_2O_7$ $1·6\sqrt{2}$ will be used instead of $4^{\frac{1}{3}}$.

Table X.

Compounds of Potassium K.

	CO_3.	SO_4.	CrO_4.	Cr_2O_7.	Cr_3O_{10}.	P_2O_6.
ΣF_e ……	7·6	8·2	7·9	11·1	14·1	10·9

Compounds of Sodium Na.

	CO_3.	SO_4.	CrO_4.	Cr_2O_7.	B_4O_7.	WO_4.	P_2O_6.	P_2O_7.
ΣF_e ……	6·4	7·1	7·0	9·9	10·3	7·8	9·9	10·3

Thus the additive principle holds throughout the values of $(M^2l)^{\frac{1}{3}}$ in Table IX. for the K and Na compounds of the monobasic acids, and in Table X. for equivalents of their compounds with dibasic acids; and if we knew the values of F for K and Na, we could at once obtain the values for the other atoms and radicals and equivalents involved. We might adopt the values already found for F for the halogens in the organic compounds, but seeing that we do not know yet how far the absolute values given by equation (2) are to be relied on, the following process is safer. From the potassium compounds we get that in $(M^2l)^{\frac{1}{3}}$, $Cl-F=1·2$, $Br-F=1·8$, and $I-F=2·7$; while in the molecular volumes M/ρ, which in solids is very nearly the same as $M\beta$, we have $Cl-F=13·9$, $Br-F=20·5$, and $I-F=30·1$; or, using mean values obtainable from data for the haloid compounds of Li, Na, K, and Rb given later on in Table XIII. from C. W. Clarke (Phil. Mag. ser. 5, iii.), we have $Cl-F=10·3$, $Br-F=16·7$, and $I-F=26·8$. It will be seen that these two series of differences in M/ρ are about ten times the corresponding differences in $(M^2l)^{\frac{1}{3}}$, and 10 was the value that we found for the ratio of B the atomic volume to F for the halogens in organic compounds: thus then it happens that equation (2), in spite of the roughnesses in it, gives values of

F for the halogens in harmony with those already found. Accordingly we could adopt for F for the halogens in inorganic compounds the values found in the organic, but it seems to me preferable to work out the results for inorganic compounds on their own basis. To do so we need the atomic volume of fluorine F. Now from the studies made by many chemists on the molecular domains (so-called volumes) of liquids at their boiling-points there have been found values carried by the individual atoms into the molecule, and for the halogens Thorpe (Journ. Chem. Soc. 1880) gives the values F=9·2, Cl=22·7, Br=28·1, and I=36·6, whence for comparison with our series of differences for the solid state we get Cl—F=13·5, Br—F=18·9, and I—F=27·4, which is curiously close to identity with our series, and indicates that we may take 9 as the atomic volume of F, so that with Clarke's differences given above we have in round numbers the following atomic volumes:—F=9, Cl=19, Br=26, and I=36, to be compared with the former Cl=19, Br=24·5, and I=32 (Table V.). Accordingly the part contributed by the fluorine atom to $(M^2 l)^{\frac{1}{2}}$ is about ·9; and with the series of differences given above we have the series of parts carried by the halogen atoms into $(M^2 l)^{\frac{1}{2}}$, namely:—

F=·9, Cl=2·1, Br=2·7, and I=3·6

to be compared with

Cl=2·2, Br=2·5, and I=3·2 in Table V.

With the above atomic volumes of the halogens and Clarke's molecular volumes of the K and Na haloid compounds given later on in Table XIII., we get the following mean atomic volumes, Na=7·4 and K=18·6; and with the above values of F for the halogens, we get from Table IX. that the mean value of F for Na is 3·1 and for K is 4·2. With these values of atomic volume and F for Na and K, we can derive from Tables IX. and X. the volumes of a number of negative radicals and their values of F when they are monobasic, of F/2 when dibasic, and of F/4 when tetrabasic. These are given in the next table.

TABLE XI.

	NO_3.	NO_2.	CN.	ClO_3.	BrO_3.
B	31 (32)	25·5 (24·5)	25 (19·5)	35	33
F	3·7 (3·2)	3·1 (2·8)	2·7 (2·4)	3·6	3·7

	CO_3.	SO_4.	CrO_4.	Cr_2O_7.	Cr_3O_{10}.	B_4O_7.	WO_4.	P_2O_6		P_2O_7.
B ...	26	34	36	76	112	70	42	67		75
F/2	3·3	4·0	3·8	6·8	9·9	7·2	4·7	6·7	F/4	4·1

The values added in brackets in the last table are reproduced from Table VI. for purposes of comparison, and show that according to our methods of calculation, for the inorganic compounds the values of F come out about 1·1 times their values as found in organic compounds (see also the values for Br and I above). This is a satisfactory result so far as it goes, but on the strength of it we will not proceed to a comparison between B and F in the last table, but will wait till we have controlled these values by an independent calculation. The data for other compounds in Table IX. are too few to be worth discussing separately, but will be considered in connexion with values by another method. The only data for the surface-tension of liquid compounds at their solidifying points known to me and not included in Table IX. are those of Traube for some compounds of Na and K with the fatty acids. These will now be briefly considered.

TABLE XII.

	K.		Na.				
	Formate.	Acetate.	Formate	Acetate.	Propionate.	Valerate.	Stearate.
am	7·1	4·3	7·7	4·0	2·3	1·4	1·4
M/ρ ...	44	61	36	53	70	104	325
$(M^2l)^{\frac{1}{3}}$ ..	6·0	6·1	5·3	5·2	5·0	5·4	14·3

These values of $(M^2l)^{\frac{1}{3}}$ are exceptional, for they do not increase by ·9 for each addition of CH_2 to the acid radical: with 4·2 for K and 3·1 for Na, also 2·9 for HCOO and ·9 for CH_2, we can calculate the following values of $(M^2l)^{\frac{1}{3}}$ for comparison with those just obtained from experiment—

7·1 8·0 6·0 6·9 7·8 9·6 21·3.

The reason for the discrepancies in these two sets of values would have to be sought for by a special inquiry.

2 (*b*). *Second Method of determining* $(M^2l)^{\frac{1}{3}}$ *for Inorganic Compounds, namely by the Kinetic Theory of Solids.*

In "A Kinetic Theory of Solids" (Phil. Mag. ser. 5, xxxii.), it was shown that, for a homogeneous isotropic solid composed of molecules which can be regarded as spheres of diameter E whose centres are at an average distance *e* from their nearest neighbours, D being the average kinetic energy of each,

$$\frac{2D}{3e^2(e-E)} - \frac{1}{6e^3}\Sigma r\phi(r) = 0. \quad . \quad . \quad . \quad . \quad (3)$$

E is also the distance apart of the centres of two when they are in contact, and $\phi(r)$ the attraction between two molecules at distance r apart, the summation to extend to all molecules within appreciable action of any one. It may be more convenient to sum both members of the above equation for all the molecules in unit mass, when we get

$$\frac{\Sigma 2\mathrm{D}}{3e^2(e-\mathrm{E})}-\frac{1}{6e^3}\Sigma\Sigma r\phi(r)=0. \quad . \quad . \quad . \quad . \quad (4)$$

If the law of force is given by $\phi(r)=3\mathrm{A}m^2/r^4$, then $\Sigma\Sigma r\phi(r)/6$ reduces to what is denoted by $l\rho$ in the notation of the "Laws of Molecular Force," and $e^3=m/\rho$, so that

$$\frac{\Sigma 2\mathrm{D}}{3e^2(e-\mathrm{E})}=l\rho^2/m \text{ and } \mathrm{M}^2l=\left(\frac{\mathrm{M}}{\rho}\right)^2\frac{\Sigma 2m\mathrm{D}}{3e^2(e-\mathrm{E})}. \quad . \quad . \quad (5)$$

This equation was established on the assumption that the molecules collide as though they were perfectly restitutional spheres.

Now $\Sigma 2\mathrm{D}$ is twice the kinetic energy of the motion of the centres of mass of the molecules in unit mass, and, if the energy of other motions is negligible, equals $2\mathrm{J}c\theta$, where θ is the temperature and c the specific heat. $e^2(e-\mathrm{E})=\mathrm{E}^3(e/\mathrm{E}-1)$ approximately; if the molecules are invariable with temperature, $e/\mathrm{E}-1=b\theta$, where b is the coefficient of linear expansion of the solid, and it was shown that the metals behave as if E diminished with rising temperature in such a way as to make $e/\mathrm{E}-1=7b\theta$ approximately; and as $\mathrm{E}^3=m/\rho$ nearly, we have

$$\frac{m\Sigma 2\mathrm{D}}{3e^2(e-\mathrm{E})}=\frac{2m\mathrm{J}c\theta}{21b\theta m/\rho}=2\mathrm{J}c\mathrm{M}/21b(\mathrm{M}/\rho), \quad . \quad . \quad (6)$$

m being the actual mass of a molecule, and M the ordinary molecular mass referred to that of the hydrogen atom. Now $c\mathrm{M}$, by Dulong and Petit's law, is nearly 6·4 for the metals, so that

$$\mathrm{M}^2l=\cdot 61\mathrm{J}(\mathrm{M}/\rho)/b. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The values of b have not been found experimentally for a number of the most interesting metals, but can be got by means of an empirical relation given in "A New Periodic Property of the Elements" (Phil. Mag. ser. 5, xxx., also xxxii. p. 540), namely, if T is the absolute melting-point $b\mathrm{TM}^{\frac{1}{2}}=\cdot 044$, and then

$$\mathrm{M}^2l=\cdot 61\mathrm{J}(\mathrm{M}/\rho)\mathrm{TM}^{\frac{1}{2}}/\cdot 044. \quad . \quad . \quad . \quad . \quad (8)$$

Taking J as $4\cdot 2\times 10^7$ ergs and using 10^{12} dynes as the unit of force as hitherto, then finally

$$\mathrm{M}^2l=5\cdot 8\times 10^{-4}(\mathrm{M}/\rho)\mathrm{TM}^{\frac{1}{2}}. \quad . \quad . \quad . \quad . \quad (9)$$

This equation applies, so far as we know at present, only to the metals; it has been deduced from (3), which applies only to solids in which the molecules are monatomic or composed of equal atoms, as in the case of the elements, all the atoms being treated as separate spheres. The corresponding equation for compound solids is sketched in section 9 of the "Kinetic Theory of Solids" (Phil. Mag. ser. 5, xxxii. p. 550), but in a form which is not correct unless a strained interpretation is put on certain symbols; but we can easily establish the correct form now. There would be no need to establish a separate form of equation for solid compounds if we knew that the molecules move as wholes; but, on the contrary, we have evidence that the atoms in the molecule move almost independently of one another, for according to Joule and Kopp's law the molecular specific heat of solid compounds is the sum of the atomic specific heats of the atoms in the molecule. In a certain sense a solid compound is like a mechanical mixture of its atoms: in the act of combining the atoms have produced mutual changes in their sizes and attracting-power and other properties, and the solid is like a mechanical mixture of these changed atoms. Now in the establishment of equation (3) for elements, the first term $2\mathrm{D}/3e^2(e-\mathrm{E})$ is calculated as the collisional pressure per unit surface, that is the force transmitted across that surface by the collisions of molecules, or rather atoms, of diameter E, average distance e from next neighbour, and kinetic enegy D, while the term $\Sigma r\phi(r)/6e^3$ is the resultant attraction which equilibrates this collisional pressure. Let N be the number of atoms in unit volume, then $e^3=1/\mathrm{N}$, and the collisional pressure can be written $2\mathrm{DN}/3(1-\mathrm{E}/e)$. Now if we have N molecules of a compound solid in unit volume, and if each molecule contains n_1 atoms of an element A_1, n_2 atoms of an element A_2, and so on, then the collisional pressure due to the n_1 atoms of A_1 in unit volume is $m_1v_1^2\mathrm{N}n_1/3(1-\mathrm{E}_1/e_1)$, and similarly for the other atoms, the total collisional pressure being their sum, so that we have the equation

$$\frac{\mathrm{N}}{3}\left(\frac{n_1m_1v_1^2}{1-\mathrm{E}_1/e_1}+\frac{n_2m_2r_2^2}{1-\mathrm{E}_2/e_2}+\ldots\right)=\frac{1}{6e^3}\Sigma r\phi(r), \quad . \quad (10)$$

denoting the mean distance of two neighbour molecules from one another by e: thus we get for a compound solid free from external force the equation

$$\frac{1}{3e^3}\left(\frac{n_1m_1r_1^2}{1-\mathrm{E}_1/e_1}+\frac{n_2m_2v_2^2}{1-\mathrm{E}_2/e_2}+\ldots\right)=\frac{1}{6e^3}\Sigma r\phi(r) \quad . \quad (11)$$

We cannot assign the values of $1-\mathrm{E}_1/e_1$ for atoms in compounds in the present state of our knowledge; but as it was shown that for the metals $1-\mathrm{E}/e=7b\theta$, where b is the coefficient of linear expansion and θ the absolute temperature, it is reasonable to imagine that in the last equation $1-E_1e_1$, $1-E_2/e_2$ and so on, can be replaced by a single mean value proportional to $b\theta$, where b is the linear coefficient of expansion of the solid compound. Denote each by $ab\theta$, where a is a constant which may or may not be the same as the 7 for metals, and replace $n_1m_1v_1^2+n_2m_2v_2^2+\ldots$, which is twice the total kinetic energy of the molecule, by its value $2JMc\theta$, where c is the specific heat of the compound, then the last equation becomes

$$\frac{2JMc}{3e^3ab}=\frac{1}{6e^3}\Sigma r\phi(r), \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

in which b is at present unknown for most compounds. But as in the metals $bTM^{\frac{1}{2}}=\cdot044$, so we may assume for compounds that $bTM^{\frac{1}{2}}$ is constant; and merging this unknown constant and $1/a$ into a single constant k, for compounds of the same type we get finally

$$M^2l=5\cdot8\times10^{-4}k\frac{Mc}{6\cdot4}(M/\rho)TM^{\frac{1}{2}}, \quad . \quad . \quad . \qquad (13)$$

differing from the equation (9) for elements only in the constant k to be ascertained for each type of compound. It so happens that for binary compounds of monad elements such as NaCl or KI, the value 1/2 for k gives good results; and as Mc for the chlorides of this type is 12·7, and for the bromides 13 8, and the iodides 13·4, the mean of which can be taken as practically double the 6·4 for the atomic specific heat of the elements, then the equation (13) for such compounds reduces to the same as that for the elements (9).

We will first take the data for the haloid compounds of the metals of the Li family; the melting-points are those given in Carnelley's paper on the Periodic Law (Phil. Mag. ser. 5, xviii., also Journ. Chem. Soc. xxix., xxxiii., xxxv., xxxvii.); the molecular domains (volumes) are those given by F. W. Clarke (Phil. Mag. ser. 5, iii.), and differ slightly from those previously given in this paper in Table IX. Below the values of $(M^2l)^{\frac{1}{2}}$ calculated by the equation (9) are given values from Table IX. found from surface-tensions.

TABLE XIII.

	Li.				Na.			
	F.	Cl.	Br.	I.	F.	Cl.	Br.	I.
T...............	1070	870	820	719	1270	1045	981	901
M/ρ	11·3	21·3	28·0	38·4	16·4	27·3	33·4	43·5
M^2l	12·0	20·0	28·0	36·2	21·2	32·5	41·1	52·4
(M^2l)	3·5	4·5	5·3	6·0	4·6	5·7	6·4	7·2
$(M^2l)^{\frac{1}{2}}$ from Table IX.	...	4·3	...	...	...	5·2	6·0	

Table XIII. (*continued*).

	K.				Rb.			
	F.	Cl.	Br.	I.	F.	Cl.	Br.	I.
T	1060	1007	972	907	...	983	956	915
M/ρ	28·2	38·3	44·6	54·3	32·6	54 8	59·5	70 3
M^2l	32·7	46·0	55·7	66·7	...	69·2	76·9	90·8
$(M^2l)^{\frac{1}{2}}$	5·7	6·8	7·5	8·2	...	8·3	8·8	9·5
$(M^2l)^{\frac{1}{2}}$ from Table IX.	5·1	6·3	6·9	7·8				

The general agreement between the two sets of values of $(M^2l)^{\frac{1}{2}}$ is surprisingly good, the values found by (9) being on the average about 7 per cent. larger than those found from surface-tensions. The data for the haloid compounds of the other metal of this family, namely Cs, are incomplete, at least I have failed to find data for the densities of Cs compounds; but the following considerations give us the molecular domains of Cs compounds in a satisfactory manner; the mean difference in the molecular domains of the corresponding Na and Li compounds is 5·4, for K and Na it is 11·2, and for Rb and K 15·8, numbers which are closely 1 × 5·4, 2 × 5·4, and 3 × 5·4. Consequently for Cs and Rb compounds we should expect a difference 4 × 5·4 or 21·6, which when added to the domains for the Rb compounds gives the domains tabulated hereunder with the melting-points taken from Carnelley's diagram:—

Table XIII. (*continued*).

	Cs.		
	Cl.	Br.	I.
T	904	879	869
M/ρ	76	81	92
M^2l	93·8	100 7	116·4
$(M^2l)^{\frac{1}{2}}$	9·7	10·0	10·8

The simplest way to deal with compounds of the type RCl_2, RCl_3, and RCl_4 is to replace $kMc/6{\cdot}4$ in equation (13) by 1, as we have done with the type RCl, and then ascertain what values must be assigned to $kMc/6{\cdot}4$ to make the results consistent with one another; then, having the value of Mc for each type, we can assign the value of k for each. As the event proves that $kMc/6{\cdot}4$ is 1, or nearly 1, for the simple types RCl, RCl_2, RCl_3, and RCl_4, we can proceed to tabulate values of $(M^2l)^{\frac{1}{2}}$ from (9), namely,

$$M^2l = 5{\cdot}8 \times 10^{-4}(M/\rho)TM^{\frac{1}{6}}, \quad . \quad . \quad . \quad . \quad (9)$$

which thus becomes the fundamental equation for the elements and the above types of compounds. For these types k therefore varies inversely as Mc, but Mc is $m_1c_1+m_2c_2+\ldots$, that is the sum of the atomic specific heats, which for most atoms are each nearly equal to 6·4, so that for these types Mc/6·4 is equal to the number of atoms in the molecule, and accordingly k is inversely proportional to the number of atoms in the molecule. When we come to types such as RNO_3, involving a compound radical NO_3, some of whose component atoms have an atomic specific heat less than 6·4, k is inversely as the number of radicals in the molecule, so that for RNO_3 it remains 1/2 as for RCl, but Mc is no longer $2\times 6{\cdot}4$. The case of $R(NO_3)_2$ is not so simple, but these matters will be gone into later on; at present we proceed with the application of (9) to the types RCl_2, RCl_3, and RCl_4.

The data and results for a number of haloid compounds of these types are given in the next table, the melting-points being as before taken from Carnelley's table and diagram, and the densities used in calculating the molecular domains being derived from various sources (chiefly F. W. Clarke's collection of data in Smithsonian Miscellaneous Collections, xii. and xiv.); the bracketed values of the molecular domains are the approximate results of interpolation.

TABLE XIV (Type RCl_2).

	Mg.				Ca.			
	F_2.	Cl_2.	Br_2.	I_2.	F_2.	Cl_2.*	Br_2.	I_2.
T	1180	981	971	889	1170	992	949	904
M/ρ	25·1	43·6	(56)	(71)	24·8	50·0	60·3	(75)
$(M^2l)^{\frac{1}{3}}$	5·8	7·3	8·6	9·7	5·9	7·9	8·9	10·0

	Sr.				Ba.			
	F_2.	Cl_2.*	Br_2.	I_2.	F_2.	Cl_2.*	Br_2.	I_2.
T	1170	1098	903	780	1180	1181	1085	929
M/ρ	(31)	51·9	62·4	77·4	36·2	54·1	70·3	(85)
$(M^2l)^{\frac{1}{3}}$	6·9	8·7	9·0	9·6	7·7	9·5	10·7	11·1

	Zn.			Cd.		
	Cl_2.	Br_2.	I_2.	Cl_2.	Br_2.	I_2.
T	535	667	719	814	844	677
M/ρ	49·4	61·8	67·9	50·5	57·9	79·4
$(M^2l)^{\frac{1}{3}}$	5·9	7·7	8·6	7·5	8·5	9·1

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* Compare with these the values in Table IX. from surface-tensions, namely, 9·8 for $CaCl_2$, 10·6 for $SrCl_2$, 12·4 for $BaCl_2$, 6·3 for AgCl, and 6·7 for AgBr, which are all about 1·2 times the values in this table, but the values of the surface-tensions are uncertain.

Table XIV.—Type RCl_2 (*continued*).

	Hg.			Hg$_2$.		
	Cl$_2$.	Br$_2$.	I$_2$.	Br$_2$.	I$_2$.	CuCl$_2$.
T…………	561	517	514	678	562	773
M/ρ………	50·0	62·7	72·4	76·6	85·1	44·0
$(M^2l)^{\frac{1}{2}}$……	6·4	7·1	7·7	9·4	9·0	6·7

	Cu$_2$.			Ag.		
	Cl$_2$.	Br$_2$.	I$_2$.	Cl.*	Br.*	I$_2$.
T…………	707	780	874	724	700	800
M/ρ ……	55·7	60·5	86·3	25·8	29·7	41·8
$(M^2l)^{\frac{1}{2}}$ …	7·4	8·4	10·8	5·0	5·4	6·9

	Pb.		
	Cl$_2$.	Br$_2$.	I$_2$.
T…………	769	769	653
M/ρ………	47·8	55·2	75·5
$(M^2l)^{\frac{1}{2}}$ ……	7·4	8·1	8·9

For the haloid compounds of other metals data are available for the boiling-point as well as for the melting-point, so that, besides the equation (9) relating to the melting-point, we can use the approximate equation ("Laws of Molecular Force," p. 247)

$$M^2l = 1190 \times 10^{-6} M v_1 T_b \quad . \quad . \quad . \quad . \quad (14)$$

relating to the boiling-point T_b, and so obtain two sets of values for $(M^2l)^{\frac{1}{2}}$, which are given in the next table along with their ratio (v_1 is strictly the volume of a gramme at T_b, but the value of $1/\rho$ at 0° C. can be taken as a good enough approximation).

TABLE XV. (Types RCl_3 and RCl_4).

	B.		Al.		C.		
	Cl$_3$.	Br$_3$.	Br$_3$.	I$_3$.	Cl$_4$.	Br$_4$.	I$_4$.
T ………………	210	270	363	398	…	364	420
T_b………………	290	363	533	623	351	462	…
M/ρ ……………	87	93	105	155	94	98	120
$(M^2l)^{\frac{1}{2}}$ from (9)…	4·8	6·1	7·5	9·9	…	7·4	9·1
$(M^2l)^{\frac{1}{2}}$ from (14)	5·5	6·3	8·1	10·7	6·3	7·3	
Ratio……………	1·14	1·03	1·08	1·08	…	0·99	

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* See footnote preceding page.

Table XV. (*continued*).

	Si.		Ti.		Sn.		
	Cl_4.	Br_4.	Cl_4.	Br_4.	Cl_4.	Br_4.	I_4.
T	...	260	...	312	260	303	419
T_b	331	426	408	503	388	474	568
M/ρ	112	124	108	142	118	132	133
$(M^2l)^{\frac{1}{2}}$ from (9)	...	7·0	...	8·3	6·7	8·0	9·7
$(M^2l)^{\frac{1}{2}}$ from (14)	6·6	7·9	7·2	9·2	7·4	8·6	9·5
Ratio	...	1·13	...	1·11	1·10	1·08	0·98

	P.		As.		
	Cl_3.	Br_3.	Cl.	Br_3.	I_3.
T	...	...	250	295	419
T_b	351	444	405	493	677
M/ρ	86	93	82	85	104
$(M^2l)^{\frac{1}{2}}$ from (9)	...	...	5·3	6·2	8·4
$(M^2l)^{\frac{1}{2}}$ from (14)	6·0	7·0	6·3	7·1	9·1
Ratio	...	...	1·19	1·15	1·08

	Sb.			Bi.	
	Cl_3.	Br_3.	I_3.	Cl_3.	Br_3.
T	345	363	438	503	480
T_b	496	549	693	703	749
M/ρ	74	88	103	69	80
$(M^2l)^{\frac{1}{2}}$ from (9)	6·0	7·0	8·6	7·2	7·8
$(M^2l)^{\frac{1}{2}}$ from (14)	6·6	7·6	9·2	7·6	8·4
Ratio	1·10	1·09	1·07	1·06	1·08

From the row of ratios it appears that the boiling-point method gives results which on the average are 1·08 times larger than those given by the melting-point, an accord which is again surprising, seeing that in an arbitrary manner we assumed for compounds the relation $T_bM^{\frac{1}{2}}=$constant, established experimentally only for the metals: if instead of ·044 we took ·040 for the constant, the agreement between the two methods would become complete for most of the compounds. This agreement proves what was asserted in connexion with equation (13), that k for these types is inversely proportional to the number of atoms in the molecule.

Before accumulating any more data it will be well to extract the general results from those just given in Tables XIII., XIV., and XV. In the haloid compounds of the Li family the mean difference in $(M^2l)^{\frac{1}{2}}$ for the chlorides and fluorides (Cl—F) is 1·1, for Br—F 1·8, and for I—F 2·5; which are a little smaller than the 1·2, 1·8, and 2·7 which we got before, although the values of $(M^2l)^{\frac{1}{2}}$ in Table XIII. are larger than those in Table IX.

Similarly we have the average values Na—Li=1·1, K—Li=2·2, Rb—Li=3·6, and Cs—Li=4·9, which go nearly as 1, 2, 3, and 4. The corresponding differences in the molecular domains with Clarke's values given in Table XIII., are Na—Li=5·4, K—LI=16·6, Rb—Li=32·4. The same molecular domains taken in conjunction with Thorpe's values for the halogens in organic compounds lead, as has been already shown, to the domains 9 for F, 19 for Cl, 26 for Br, and 36 for I, which lead to a mean value 2·0 for Li; so that the molecular domains of the metals of the Li family in the compound state are 2·0 for Li, 7·4 for Na, 18·6 for K, 34·4 for Rb, and probably 56 for Cs. To obtain the values contributed to $(M^2l)^{\frac{1}{2}}$ by these atoms, it must be remembered that from the results in Table IX. we found that the value for fluorine might be taken as ·9, so for the numbers in Table XIII. it should be taken as about ·9, giving for the halogens the values ·9 for F, 2·0 for Cl, 2·7 for Br, and 3·4 for I, nearly the same as the former values ·9, 2·1, 2·7, and 3·6; which will be retained and lead to the values 2·4 for Li, 3·5 for Na, 4·6 for K, 6·0 for Rb, and 7·3 for Cs, which go very nearly as 2, 3, 4, 5, and 6.

To complete the data for the Be family we require the densities of the haloid compounds of Be, but as these appear to be wanting we must approximate to the molecular volumes of the Be compounds by means of the fact that the molecular volume of BeO is 5 less than that of MgO; subtracting then 5 from the molecular volumes of $MgCl_2$, $MgBr_2$, and MgI_2, we can supply the following

Supplement to Table XIV.

Be.

	Cl_2.	Br_2.	I_2.
T	870	870	770
M/ρ	39	51	66
$(M^2l)^{\frac{1}{2}}$	6·4	7·8	3·6

On passing from the haloid compounds of the monad metals in Table XIII. to the compounds of the dyads, triads, and tetrads in Tables XIV. and XV., the first point to arrest attention is that the values for $I_2—Cl_2$, $I_3—Cl_3$, $I_4—Cl_4$ are not 2 and 3 and 4 times the value of I—Cl already found in connexion with the monad metals: we have the following mean values:—

I—Cl.	I_2—Cl_2.	I_3—Cl_3.	I_4—Cl_4.
1·4	1·8	2·7	3·1

The discrepancies in these values might be ascribed to an error in the assumption that $kMc/6{\cdot}4$ is equal to the same constant 1 for all these types of compounds; and it might be supposed that the constant ought in each case to be chosen so that I_2—Cl_2, I_3—Cl_3, and I_4—Cl_4 are 2 and 3 and 4 times I—Cl. But this supposition breaks down when it is remembered that in the types RCl_3 and RCl_4 values of $(M^2l)^{\frac{1}{3}}$ as found by the independent boiling-point method are only 8 per cent. larger than those by the other method. It is true that the boiling-point method is only approximate, but that the approximation is fairly close can be seen by comparing the following pairs of values, the first of each pair being the approximate value from Table XV. and the second the value from Table VII., namely:—

PCl_3.	$AsCl_3$.	CCl_4.	$SiCl_4$.	$SnCl_4$.
6·0	6·3	6·3	6·6	7·4
6·6	7·0	6·8	6·9	7·8

These comparisons show that the phenomenon that the values in $(M^2l)^{\frac{1}{3}}$ for I—Cl, I_2—Cl_2, I_3—Cl_3, and I_4—Cl_4 do not stand as 1, 2, 3, 4 is a real one, and not the result of accumulated imperfections in the methods of calculation. The values given above for these differences stand more nearly in the relation 1, $2^{\frac{1}{3}}$, $3^{\frac{1}{3}}$, $4^{\frac{1}{3}}$; and supposing it to be the true one, they can be brought into almost complete harmony if we return to the old relation $bTM^{\frac{1}{3}}$=constant, and denoting by E an equivalent replace it by $bTE^{\frac{1}{6}}$=constant, which would reduce the values of $(M^2l)^{\frac{1}{3}}$ for the four types in Tables XIII., XIV., and XV. by factors 1, $1/2^{\frac{1}{12}}$, $1/3^{\frac{1}{12}}$, $1/4^{\frac{1}{12}}$: then the numbers 1·4, 1·8, 2·7, and 3·1 for I—Cl, I_2—Cl_2, I_3—Cl_3, and I_4—Cl_4 ought to be as 1, $1/2^{\frac{7}{12}}$, $1/3^{\frac{7}{12}}$, and $1/4^{\frac{7}{12}}$. Dividing the numbers by these powers, we get for I—Cl the series of values 1·4, 1·2, 1·4, and 1·4, which are as nearly constant as possible under the circumstances.

This constitutes the main part of the proof that in compounds of the type RS_n, where R is an n-valent atom and S a monad, $(M^2l)^{\frac{1}{3}}$ is of the form $(F_r+nF_s)/n^{\frac{1}{3}}$, whence $(M^2l)^{\frac{1}{3}}/n^{\frac{1}{3}}=F_r/n+F_r$. Thus our best plan will be to divide the numbers in Table XIII. by $2^{\frac{1}{12}}$, and those in XIV. by

$3^{\frac{1}{3}}$ and $4^{\frac{1}{3}}$, and tabulate the results as $F_r/2+F_s$, $F_r/3+F_s$, and $F_r/4+F_s$, according to the type of compound.

TABLE XVI.—($F_r/2+F_s$).

	Be.	Mg.	Ca.	Sr.	Ba.
F_2	...	3·9	3·9	4·6	5·1
Cl_2	4·2	4·8	5·3	5·8	6·3
Br_2	5·2	5·8	5·9	6·0	7·1
I_2.........	5·7	6·4	6·7	6·4	7·4

There are some irregularities among these numbers, the most pronounced being where the value for SrI_2 falls below that for CaI_2; but ignoring these as due to no fundamental error, we get, taking the data for the chlorides as the best, with 2·1 as the value for Cl, the following values for $F_r/2$ or $F/2$, and approximate values of B derived from the best values of M/ρ in Table XIV.

TABLE XVII.

	Be.	Mg.	Ca.	Sr.	Ba.
F/2=	2·1	2·7	3·2	3·7	4·2
B =	1·0	5·6	8·6	10·6	16·6

Table XVI. (*continued*).—$F_r/3+F_s$.

	B.	Al.	P.	As.	Sb.	Bi.
Cl_3	2·7	...	2·9	3·0	3·2	3·7
Br_3	3·1	4·0	3·4	3·4	3·7	4·1
I_3	...	5·2	...	4·5	4·5	

Table XVI. (*continued*).—$F_r/4+F_s$.

	C.	Si.	Ti.	Sn.
Cl_4	2·6	2·7	3·0	3·0
Br_4	3·1	3·2	3·8	3·5
I_4	4·0	...	...	4·1

The values just given for the types RCl_3 and RCl_4 are the means of those given by both the melting-point and boiling-point methods, the latter being reduced first by dividing by 1·08 the mean ratio of results by the two methods, and then converted to equivalent values by dividing by $3^{\frac{1}{3}}$ and $4^{\frac{1}{3}}$.

Again, amongst the types RCl_3 and RCl_4, taking the values of $F_r/3+F_s$ and $F_r/4+F_s$ for the chlorides as the most reliable, but allowing for the others where necessary, and using 2·1 as the value of F_s for Cl as S, we get the approximate values :—

TABLE XVIII.

	P.	As.	Sb.	Bi.	B.	Al.		C.	Si.	Ti.	Sn.
F/3...	·8	·85	1·05	1·5	·6	1·2	F/4...	·5	·6	·95	·95

In the compounds of the zinc family irregularities appear in $(M^2l)^{\frac{1}{2}}$: thus for I_2-Cl_2 we get with Zn 2·7, with Cd 1·6, and with Hg(ic) 1·3, instead of the 1·8 proper to dyads : so also are the compounds of Cu(ous) and Ag exceptional, for $Cu_2I_2-Cu_2Cl_2$ is 3·4 and $AgI-AgCl$ is 1·9; but the reasons for these irregularities can hardly be gone into in the present paper, though in a general way they suggest themselves.

So far the method of the Kinetic Theory of Solids has been applied to only the haloid compounds of the metals, and it will be interesting to see how it works with compounds involving more complicated acid monovalent radicals such as NO_3, ClO_3. The equation (13), which for the haloid compounds was shown to simplify down to (9), must for these compounds be used in its original form (13) with $k=1/2$: for the nitrates of the form RNO_3, Mc has a mean value 24, so that (13) becomes

$$M^2l=5{\cdot}8\times\frac{24}{12{\cdot}8}(M/\rho)TM^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \qquad (15)$$

which will be used as near enough for the chlorates, bromates, and iodates, though in them Mc is a little larger. The following are the data for this type of compound :—

TABLE XIX.

Nitrates.

	Li.	Na.	K.	Ag.	Tl.
T.........	540	693	605	491	478
M/ρ ...	28·9	39·0	48·8	39·2	45·9
$(M^2l)^{\frac{1}{2}}$...	5·8	7·1	8·3	7·0	7·8

	Chlorates.		Bromates.		Iodates.	
	Na.	K.	Na.	K.	Na.	K.
T	575	632	654	(690)	(770)	833
M/ρ	43·0	52·8	45·2	51·2	46·3	55·0
$(M^2l)^{\frac{1}{2}}$ ...	7·9	8·9	8·6	9·5	9·7	11·0

With the values 2·4 for Li in $(M^2l)^{\frac{1}{2}}$, 3·5 for Na, and 4·6 for K obtained from the haloid compounds, we derive from the last table the following mean values for the parts contributed by the radicals NO_3, ClO_3, BrO_3, and IO_3 to $(M^2l)^{\frac{1}{3}}$, along with the values reproduced from Table XI., where they were obtained by the surface-tension method :—

TABLE XX.

NO_3.	ClO_3.	BrO_3.	IO_3.
3·6	4·4	5·0	6·3
3·7	3·6	3·7	

The agreement in the two sets of values is good only for NO_3, but it should be noted that the value for BrO_3 from Table XI. is too small in comparison with that for ClO_3. With 3·6 as the value for NO_3 we can obtain from Table XIX. values for Ag and Tl, namely Ag = 3·4, which is ·1 less than Na, while the irregular results for the haloid compounds of Ag would make it about ·5 less ; for Tl the value is 4·2.

To the data for the carbonates, sulphates, and metaphosphates of the monad metals similar considerations have to be applied as to those for the nitrates. Equation (13) has to be used with a value 28 for *Mc* in the carbonates of type R_2CO_3, 33 in the sulphates R_2SO_4, and 50 in the metaphosphates. As there are 3 radicals in these types *k* will be 1/3, and as in the case of RCl_2 we divided our original values of $(M^2l)^{\frac{1}{3}}$ by $2^{\frac{1}{3}}$ to get true values of $(M^2l)^{\frac{1}{3}}/2^{\frac{1}{3}}$ or ΣF_e, so also in these types we must do the same : thus for the carbonates R_2CO_3,

$$M^2l = 5{\cdot}8 \times 10^{-4} \times \frac{28}{3 \times 6{\cdot}4 \times 2^{\frac{1}{3}}} ; \quad . \quad . \quad . \qquad (16)$$

for the sulphates R_2SO_4,

$$M^2l = \text{the same with 33 in place of 28,}$$

and for the metaphosphates the same with 50 in place of 28. These equations give the following values :—

TABLE XXI.

Carbonates.

	Li.	Na.	K.	Rb.	Tl.
T	968	1087	1107	1110	546
M/ρ	35	43	60	(92)	66
ΣF_e	5·1	6·2	7·6	9·7	6·1

	Sulphates.					Metaphosphates.	
	Li.	Na.	K.	Ag.	Tl.	Na.	Ag.
T	1001	1134	(1150)	927	905	890	755
M/ρ	50	54	66	58	74	82	84
ΣF_e	7·3	7·8	8·9	7·9	9·2	10·9	10·7

The value of ΣF_e for Tl_2CO_3 is probably too small because the melting-point given for this compound seems to be too low. Confining our attention to the Na and K data, which are the best, we get for F/2 for CO_3 the value 2·8 as against 3·3 by the surface-tension method, and for SO_4 F/2 is 4·3 as against 4·0 in the surface-tension method. This value 4·3 gives for F in Ag a value 3·6, while 3·4 was the value derived from the nitrate, in Tl F is 4·9 from the sulphate as against 4·2 from the nitrate; the values for the metaphosphates again show that Na and Ag have nearly equal values for F, and that for P_2O_6 F/2 is 7·4, while 6·7 was the value found by the former method.

We advance to a higher degree of molecular complexity when we take up the nitrates of the dyad metals of type $R(NO_3)_2$; here M*c* is 41·6, and as there are three radicals in the molecule *k* is 1/3, and thus

$$M^2l = 5{\cdot}8 \times 10^{-4} \frac{41{\cdot}6}{3 \times 6{\cdot}4} (M/\rho)TM^{\frac{1}{3}} \quad . \quad . \quad . \quad . \qquad (17)$$

It happens that this equation, when applied as in the next Table to the nitrates of Ca, Sr, and Ba, gives values for $(M^2l)^{\frac{1}{2}}$ which are nearly the sum of F for Ca and twice F for NO_3, and so on, so that the effect of valency does not appear here; but before remarking further about this let us take the data :—

TABLE XXII.

	Nitrates.		Chlorates.	
	Ca.	Sr.	Ba.	Ba.
T	834	918	866	687
M/ρ	69·5	71·9	80·9	(97)
$(M^2l)^{\frac{1}{2}}$	13·0	14·2	14·9	14·7

With F for NO_3 as 3·6, for Ca as 6·4, Sr 7·4, and Ba 8·4 (see Table XVII.), we get for the nitrates 13·6, 14·6, and 15·6, when valency is ignored, and these values are in substantial agreement with those just given in the Table. The question arises whether this is merely the fortuitous effect of some peculiarity of these nitrates not taken account of in equation (17), or whether it is due to the fact that the valency of the atom which determines the type exercises less influence as the radicals to which it is united become more complex; or, in other words, do the compounds of the metals when complex enough tend towards obeying the same law for $(M^2l)^{\frac{1}{2}}$ as holds in the carbon compounds? The question is merely raised in connexion with the results of the last table, to which by themselves little weight need be attached, but we will return to the matter shortly in connexion with the organometallic compounds. Meanwhile we will take the data for a few compounds of tri- and tetrabasic acids with which to gain some more knowledge of the influence of the basicity of an acid radical on its attracting-power; these compounds are Li_3PO_4 and Ag_3PO_4, the orthophosphates of Li and Ag, $Na_4P_2O_7$ and $Ag_4P_2O_7$, the pyrophosphates of Na and Ag, and along with these will be taken $Na_2B_4O_7$, the Na salt of the dibasic pyroboric acid.

For the orthophosphates $Mc=41$, for the pyrophosphates 63, and for the pyroborate 63; in the orthophosphates there are four radicals to the molecule, so that $k=1/4$, so for the pyrophosphates $k=1/5$, and for the pyroborate $k=1/3$: thus the equation (13) becomes for the orthophosphates

$$M^2l=5\cdot8\times10^{-4}\times\frac{41}{4\times6\cdot4}\,(M/\rho)TM^{\frac{1}{2}}, \quad . \quad . \quad . \quad (18)$$

and so on. To reduce $(M^2l)^{\frac{1}{2}}$ to ΣF_e, we must divide it by $3^{\frac{1}{12}}$ for the orthophosphates, by $4^{\frac{1}{12}}$ for the pyrophosphates, and by $2^{\frac{1}{12}}$ for the pyroborate; and thus we get

Table XXIII.

	Li_3PO_4.	Ag_3PO_4.	$Na_4P_2O_7$.	$Ag_4P_2O_7$.	$Na_2B_4O_7$.
T	1130	1122	1161	858	834
M/ρ ...	(50)	(68)	109	113	85
ΣF_e ...	5·8	7·5	8·5	8·0	12·0

With 2·4 as the value of F for Li, and 3·4 for Ag, we get that for PO_4, F/3 is 3·4 and 4·1, or in the mean 3·7; so with 3·5 for Na and 3·4 for Ag, F/4 for P_2O_7 is 5·0 and 4·6, or 4·8 in the mean; so also F/2 for B_4O_7 is 8·5, the value found by the surface-tension method for F/2 in B_4O_7 was 7·2, and for F/4 in P_2O_7 was 4·1 (see Table XI.), which would be obtained on dividing the values just found by 1·2.

We are now in a position to make the same comparison between the values of F for a large number of acid radicals in inorganic compounds, and the volumes B of these radicals, as was made in connexion with organic compounds. In the following Table the first row contains the value of F as given by the surface-tension method in Table XI., in the second row the values of F given by the Kinetic Theory of Solids, in the third the mean of these two sets of values, in the fourth the volumes of the radicals deduced from those of their compounds given in previous tables, and in the fifth the ratio of B to F.

TABLE XXIV.

Monobasic Acid Radicals.

	NO_3.	NO_2.	CN.	ClO_3.	BrO_3.	IO_3.
F from Ta. XI...	3·7	3·1	2·7	3·6	3·7	
F Kin. Th.	3·6	...	...	4·4	5·0	6·3
F mean	3·6	3·1	2·7	4·0	4·4	6·3
B	31	25·5	25	35	33	39
B/F	8·5	8	9	9	7·5	6

The values of the ratio for NO_3, NO_2, and CN, namely 8·5, 8, and 9, are not far from the mean value 10 found for the same ratio in organic compounds: for these three radicals the values of the ratio in Table VI. were 10, 9, and 8; for ClO_3 the ratio in the last table is 9, but for BrO_3 it falls to 7·5, and for IO_3 to 6. This is due to the values of B for these radicals being smaller than they ought to be if regular, for B for BrO_3 instead of being less than for ClO_3 ought to be 6·4 greater, which would make it 41, and bring the ratio up to 9; similarly B for IO_3 ought to be 16·5 greater than that for ClO_3, which would bring it up to 51, and make the ratio 8.

Table XXIV. (*continued*).

Dibasic Acid Radicals.

	CO_3.	SO_4.	CrO_4.	Cr_2O_7.	Cr_3O_{10}.	P_2O_6	B_4O_7.	WO_4.
F/2 from Ta XI...	3·3	4·0	3·8	6·8	9·9	6·7	7·2	4·7
F/2 Kin. Th.	2·8	4·3	...	..	...	7·4	8·5	...
F/2 mean............	3·0	4·1	3·8	6·8	9·9	7·0	7·8	4·7
B	26	34	36	76	112	67	70	42
2B/F..................	8·5	8	9	11	11	9·5	9	9

This part of the table shows that for the dibasic acid radicals the ratio 2B/F is constant within the limits of accuracy attainable; and the remarkable fact appears that 2B/F for the dibasic acid radicals has the same value as B/F for the monobasic. There is only one datum for a tribasic acid and one for a tetrabasic, namely,

Table XXIV. (*continued*).

	PO_4.	P_2O_7.	
		4·1	F/4 from Ta. XI.
F/3 Kin. Th.	3·7	4·8	F/4 Kin. Th.
F/3 mean	3·7	4·4	F/4 mean.
B....................	44	75	B.
3B/F	12	17	4B/F.

For the tribasic acid radical the ratio 3B/F is 12, and therefore 2B/F is 8; for the tetrabasic radical 4B/F is 17, and therefore 2B/F is 8·5; and both these values for 2B/F range themselves with the values found for 2B/F in the dibasic radicals. This, then, is a noteworthy result, that for all acid radicals of a basicity higher than 1 the ratio 2B/F is nearly constant, and has half the value of the same ratio for radicals of basicity 1. This recalls the result we found before, that for atoms in organic compounds the ratio B/F has a value nearly half of that for the elements and CH_4, C_2H_4, and CH_2. Our results for the acid radicals may be summed up in the two formulas—$B=9F$ nearly in the unibasic, $2B=9F$ nearly in the polybasic.

The last compounds to be considered briefly in the present paper are the organometallic, for which M^2l can be calculated by the equation (14),

$$M^2l=1190\times10^{-6}Mv_1T_b,$$

with the data collected by Carnelley (Phil. Mag. 5th ser. xx. p. 260), namely, the boiling-points and densities at about 15° C. of various methides, ethides, and so on. In the following table these data are not reproduced, but only the values of M/ρ and $(M^2l)^{\frac{1}{2}}$ calculated from them. The types of compound are indicated by the headings ZnR_2, SnR_4, and so on, R being CH_3 in the first row, and so on.

TABLE XXV.

	ZnR_2.		HgR_2.		SnR_4.		PbR_4.	
	$(M^2l)^{\frac{1}{2}}$.	M/ρ.	$(M^2l)^{\frac{1}{2}}$.	M/ρ.	$(M^2l)^{\frac{1}{2}}$	M/ρ.	$(M^2l)^{\frac{1}{2}}$	M/ρ.
$R=CH_3$	5·1	68	5·7	75	7·5	136	8·2	130
C_2H_5......	6·9	104	7·4	106	10·3	197	10·6	202
C_3H_7......	8·4	137	8·6	135	12·0	263	—	—
	Br_3.		SiR_4.		NR_3.		PR_3.	
CH_3	—	—	—	—	—	—	—	—
C_2H_5......	7·8	140	9·7	187	7·7	138	8·3	146
C_3H_7......	—	—	12·3	263	—	—	—	—
C_4H_9......	—	—	—	—	11·7	237	—	—
	AsR_3.		SbR_3.		OR_2.		SR_2.	
CH_3	—	—	6·8	110	—	—	5·2	74
C_2H_5......	8·5	140	9·0	158	6·1	101	6·8	107
C_3H_7......	—	—	—	—	—	—	8·3	145
C_4H_9......	—	—	—	—	9·1	169	9·7	174
	ClR.		BrR.		IR.			
CH_3	—	—	4·3	57	—	—		
C_2H_5......	4·8	69	5·2	74	5·7	80		
C_3H_7......	5·7	87	6·0	89	6·6	97		

The values for compounds of O, S, Cl, Br, and I have been introduced into the table only to give an idea of the degree of approximateness of the values in the table, for more accurate values for these compounds have been already discussed. First let us consider the values of M/ρ which may be taken as $M\beta$.

These numbers show that in $M\beta$ CH_2 has a value about 16·5, which is close to the limiting domain for CH_2 in the organic compounds, though it ought to be larger, seeing that the density ρ used in the organometallic compounds is not the limiting density, but that of the liquids about 15° C. We will take the value for H to be the same as in the organic compounds, namely 4·5, and then CH_3 is 21, C_2H_5 is 37·5, C_3H_7 is 54, and C_4H_9 is 70·5; with which we get the following mean values of the atomic domains of the metals in the organometallic compounds:—

Zn.	Hg.	Sn.	Pb.	Si.	P.	As.	Sb.
28	30	49	49	42	33·5	27·5	46

Except for P and As, these domains are much larger than in the inorganic compounds: for instance, the domain of $PbCl_2$ is only 47·8, which is actually less than the domain of Pb in the organic compounds. Of course the one number is calculated for the solid state, and the other for the liquid, but this could explain only a small part of the discrepancy. There is no doubt that the metallic atoms occupy more space in the organic than in the inorganic compounds; in the inorganic compounds Sb may be seen to have a domain about 20, while in the organic compounds the value is 46. This is a very significant fact, that seems not to have been noticed by those who have occupied themselves with the question of molecular domains (volumes).

As regards $(M^2l)^{\frac{1}{2}}$, we know that in organic compounds CH_2 has a value ·9, which is the value it possesses amongst the chlorides, bromides, and iodides of the last table; but in the metallic compounds the values are smaller. In the Zn compounds $2CH_2$ has the values 1·8 and 1·5, with Hg 1·7 and 1·2; in the Sn compounds $4CH_2$ is 2·8 and 1·7, and in the Pb compounds 2·4: in every case the greater the number of CH_2 groups the smaller the value of CH_2; the compounds of S show the diminution clearly, for they give for CH_2 instead of 1·8 the values 1·6, 1·5, 1·4. These results seem to show that the approximate equation (14), used to calculate the values of $(M^2l)^{\frac{1}{2}}$ in Table XXV., gives less and less accurate results the more complex the molecule becomes, but at the same time they show that as the value for CH_2 between the methides and ethides is not far from the truth, the values for the methides may be taken as nearly correct, and where a value for the methide is wanting an approximate one can be got by subtracting from the value for the ethide ·75 for each CH_2. Thus we get the following Table for the methides only:—

TABLE XXVI.

	$ZnMe_2$.	$HgMe_2$.	$SiMe_4$.	$SnMe_4$.	$PbMe_4$.	BMe_3.	NMe_3.	PMe_3.
$(M^2l)^{\frac{1}{3}}$.	5·1	5·7	6·7	7·5	8·2	5·6	5·5	6·1

	$AsMe_3$.	$SbMe_3$	OMe_2.	SMe_2.	ClMe.	BrMe.	IMe.
$(M^2l)^{\frac{1}{3}}$.	6·3	6·8	4·6	5·2	4·0	4·3	5·0

Here again values are given for the methides of N, O, S, Cl, Br, and I, only as checks. The first point to ascertain is whether in the true metallic methides $(M^2l)^{\frac{1}{3}}$ follows the laws proper to organic compounds or inorganic metallic compounds. In the organic compounds CH_2 has a value ·9, and the other H of CH_3 a value 1·1, so that CH_3 is 2, and thus the values for $SiMe_4$ and $SnMe_4$ are less than for Me_4: therefore the organometallic compounds do not behave as ordinary organic compounds; but as we have seen the valency of the metallic atoms play an important part in the values of $(M^2l)^{\frac{1}{3}}$ for their inorganic compounds, it will be best to try the effect of treating the methides as we did the metallic chlorides and similar compounds. That is, we must divide the values of $(M^2l)^{\frac{1}{3}}$ in Table XXVI. by $n^{\frac{1}{3}}$, where n is the valency of the metallic atom; then, subtracting 2 for CH_3 from each of the results, we get the values of F/n for the metallic atoms. These are given in the first row of the following table, the second row containing the values from Table XVIII.

TABLE XXVII.

	Zn.	Hg.	Si.	Sn.	Pb.	B.	N.	P.	As.	Sb.
F/n	1·6	2·1	1·35	1·75	2·1	1·2	1·2	1·5	1·55	1·9
F/n from Ta. XVIII.	...	...	·6	·95	...	·6	...	·8	·85	1·05

It appears that the values of F for the metallic atoms in the organometallic compounds are double the values in the inorganic compounds, whether the atoms are dyad, triad, or tetrad; and this seems to correspond closely with what we found in the study of the ratio B/F for the compound acid radicals, because for basicities higher than one this ratio came out only half the value for basicity one, which corresponds to a value of F double what would be expected from other considerations. As these facts show a characteristic influence belonging to compound radicals, it will be instructive to return to the case of the nitrates of the dyad metals, in which, according to what we have just seen, the values of $(M^2l)^{\frac{1}{2}}$ in Table XXII. when divided by $2^{\frac{1}{2}}$ and reduced by 3·6, the value for NO_3, ought to leave values for F/2 for Ca, Sr, and Ba which are double the values obtained from the halogen compounds. Performing these operations we get for

	Ca.	Sr.	Ba.
F/2	5·1	5·9	6·3
From Table XVII.......	3·2	3·7	4·2

The values of F/2 from the nitrates are only 1·5 and not 2 times the values from the chlorides; and thus the nitrates of these metals do not come satisfactorily under this principle, and there are too many steps in the process of determining the value of F/2 from the nitrates to enable us to fix upon a probable cause of the discrepancies in these nitrates.

With the organometallic compounds we have finished the data for compounds to be discussed in the present paper, and have now an opportunity to make a comparison between the values contributed by the atoms of the metals to $M\beta$ and to $(M^2l)^{\frac{1}{2}}$ in a molecule, though to keep it clear that in the compounds of the metals we have had to take account of valency n we will give the values of B/n and F/n in the following table. There is considerable difficulty in getting the atomic volumes of such atoms as P and As, because the relations of the chlorides, bromides, and iodides are not consistent with those of the chlorides, bromides, and iodides of the monad metals; the volumes of the lower members of the monad and dyad series are also difficult to assign, being small. In the case of P, As, and Sb the volumes adopted are those given by Thorpe (Journ. Chem. Soc. 1880) as the domains of these atoms in liquids at their boiling-points; they are therefore probably too large, but not necessarily much too large, because the domains of the halogens in organic compounds at their boiling-points are almost identical with their limiting volumes in these compounds, and also in metallic compounds. Accordingly the values of the limiting volumes of the atoms given in the next table are only such general approximate values as represent best the facts of the simplest compounds.

TABLE XXVIII.

	Li.	Na.	K.	Rb.	Cs.	Be.	Mg.	Ca.	Sr.	Ba.
F/n.........	2·4	3·5	4·6	6·0	7·3	2·1	2·7	3·2	3·7	4·2
B/n.........	2	7·4	18·6	34·4	56·0	·5	2·8	4·3	5·3	8·3

	P.	As.	Sb.	Bi.	C.	Si.	Ti.	Sn.
F/n.........	·8	·85	1·05	1·5	·5	·6	·95	·95
B/n.........	8·3	8·7	9·7	...	2·7	7·5	8·5	10·0

A glance at the numbers for the Li and Be families of metals shows that the ratio of B to F is not constant, as we found to be approximately the case with non-metallic atoms and radicals; but when we get to the families which are half non-metallic and half metallic, as in the P family and the C family, we see that the ratio, except in the case of C itself, is not far from 10, the value which we have hitherto found for non-metallic atoms and radicals. For further assurance as to the reality of this distinction between metals and non-metals, the best course will be to determine values of M^2l for the uncombined metals.

3. *Determination of* M^2l *for the Uncombined Elements.*

Data are available for both methods of calculating M^2l, and that of the Kinetic Theory of Solids will be taken first as being applicable to a greater number of substances. At first the molecular mass will be regarded as unknown, and for M the usual atomic weight will be used in equation (9). The following table contains the values of T the melting-point and of M/ρ from L. Meyer's 'Modern Theories of Chemistry,' and the values of M^2l [not $(M^2l)^{\frac{1}{3}}$] calculated from them by equation (9), as well as the values of the ratio $(M/\rho)/M^2l$ [not $(M/\rho)/(M^2l)^{\frac{1}{3}}$]. Equation (9) applies strictly only to the metals, but in a formal manner it is here extended to some non-metals.

TABLE XXIX.

First family and Copper subfamily.

	Li.	Na.	K.	Rb.	Cs.	Cu.	Ag.	Au.
T	453	369	335	311	300	1330	1230	1310
M/ρ............	11·9	23·7	45·4	56·1	70·6	7·2	10·2	10·2
M^2l	4·1	8·6	16·2	21·2	27·6	11·1	15·9	18·7
$(M/\rho)/M^2l$ ...	2·9	2·8	2·8	2·6	2·6	·65	·64	·55

Second family and Zinc subfamily.

	Be.	Mg.	Ca.	Sr.	Ba.	Zn.	Cd.	Hg.
T..............	1230	1023	900	800	748	690	590	234
M/ρ............	5·6	13·8	25·4	34·9	36·5	9·1	12·9	14·7
M^2l	5·8	13·9	24·5	34·0	35·9	7·3	9·7	4·8
$(M/\rho)/M^2l$ ...	1·0	1·0	1·0	1·0	1·0	1·25	1·33	3·0

Table XXIX. (*continued*).

Third family and Gallium subfamily.

	Al.	La.	Ga.	In.	Tl.
T	1123	710	303	449	563
M/ρ	10·6	22·3	11·7	15·3	18·1
M^2l	11·9	23·5	4·1	8·8	14·3
$(M/\rho)/M^2l$ ...	·9	·95	2·8	1·75	1·25

Fourth family and Tin subfamily.

	Ce.	Sn.	Pb.
T	1000	503	599
M/ρ	21·0	16·1	18·1
M^2l	27·9	10·9	15·3
$(M/\rho)/M^2l$............	·75	1·5	1·2

Fifth family and Arsenic subfamily.

	P.	Di.	As.	Sb.	Bi.
T	420 (mean)	1200	773	710	540
M/ρ	13·5	22·3	13·2	17·9	21·1
M^2l.................	5·8	35·7	12·2	16·4	16·1
$(M/\rho)/M^2l$.........	2·3	·62	1·1	1·1	1·3

Sixth family.

	S.	Se.	Te.
T	388	490	728
M/ρ	15·7	17·1	20·2
M^2l	6·3	10·0	19·0
$(M/\rho)/M^2l$	2·5	1·7	1·06

Seventh family.

	Cl.	Br.	I.
T	198	266	387
$M\beta$	17	22	25·6
M^2l	3·5	7·0	12·9
$(M\beta)/M^2l$	4·9	3·1	2·0

Eighth family—Iron, Palladium, and Platinum groups.

	Fe (Ni Co).	Pd (Ru Rh).	Pt (Os Ir).
T	2080	1775	2050
M/ρ	7·2	9·2	9·1
M^2l	16·9	20·6	26·1
$(M/\rho)/M^2l$	·42	·45	·35

The first point of importance brought out by this table is that in the main families the ratio $(M/\rho)/M^2l$ has a constant value characteristic of each family, and in the subfamilies a value simply related to that of the main family: thus in the first family the range in the value of the ratio is only from 2·9 for Li to 2·6 for Cs, with a mean value 2·7, of which the value for Cu and Ag in the subfamily is a quarter. In the second family the ratio is constant from Be to Ba with a value 1·0, but the mean value 1·3 for Zn and Cd in the subfamily is greater than that of the main family, which is in strong contrast to the behaviour of the copper subfamily, and may have some significance, as will be seen presently; the distinct manner in which Hg separates itself with a value 3 should be noticed. In the third family there are only two members, Al and La, which both have the same value for the ratio, ·9, and in the subfamily Ga has 3 times this value, in which respect it is similar to Hg, and In has double the value of the main family, Tl has perhaps 1·5 times that of the main family. In the fourth family there is only one main representative Ce with a value ·75, of which that for Sn is exactly double, as was the case with In and the third family; the value for Pb appears, like that of Tl, to be 1·5 times the value of the main family. In the fifth family a certain arbitrariness in our separation into main and sub-families becomes apparent, because P, As, Sb, and Bi have the close relationships of a main family; Di, which is the only metallic representative of the fifth family, has a value ·62 for the ratio, of which those for As, Sb, and Bi are double, and that for P is again double those for As, Sb, and Bi. In the sixth and seventh families, where the metallic character disappears, regularities in the ratio $(M/\rho)/M^2l$ disappear, but in these non-metallic elements the tendency is towards M/ρ being proportional to $(M^2l)^{\frac{1}{2}}$ and not to M^2l. In the eighth family the ratio $(M/\rho)/M^2l$ has a mean value ·41.

The second point of importance brought out by Table XXIX. is that the ratio $(M/\rho)/M^2l$ for each main family exhibits a remarkable relationship to the valency of the family when the main family is metallic. This is shown in the next table, where the first row contains the valency of the family, the second the value of the ratio $(M/\rho)/M^2l$ for the family, and the third the product of these two.

Table XXX.

Valency of family	1	2	3	4	5	8
Ratio	2·7	1·0	·92	·75	·62	·41
Product of valency and ratio ...	2·7	2·0	2·8	3·0	3·1	3·3

This table shows that if n is the valency, or perhaps it is safer to say the *order* of the main family, then $n(M/\rho)/M^2l$

shows a close approach to constancy, except in the case of the second family, whose place seems to be taken by the dyad zinc subfamily, in which the ratio $(M/\rho)/M^2l$ is 1·3, and therefore the product $n(M/\rho)/M^2l$ is 2·6. As the subfamilies have a ratio $(M/\rho)/M^2l$, which is a simple multiple or submultiple of the value in the main family, we can say that in the metals $n(M/\rho)/M^2l$ is close to 2·8, or a simple multiple or submultiple of 2·8, except in the second family, where it is 2·0. Thus the attracting-power of a metallic atom is proportional to the square root of its volume or of a simple multiple of its volume, and also to the square root of its valency. This relation for the metals can also be stated in another interesting form, for as $l\rho$ represents the potential energy due to the attractions of the molecules in unit mass, $M^2l/(M/\rho)$ is the potential energy of mass M, which may be taken as forming the greater part of the heat of vaporization of the gramme-molecule; thus, then, the potential energy of the molecules in a gramme-equivalent (and probably the latent heat of vaporization of a gramme-equivalent) of the metals in the main families has nearly the same value for all, and in the other metals a value which is a simple multiple or submultiple of this. The methods devised in this paper for calculating M^2l for inorganic compounds also lead to approximate values of their latent heats of vaporization, which are of some importance in Thermochemistry.

With this knowledge of the relation between M^2l and volume in the uncombined metals, we can return to the study of the relationship of the parts carried by the metallic atoms into $(M^2l)^{\frac{1}{2}}$ and $M\beta$. We have already seen that the metallic atoms in combination do not have their parts of $(M^2l)^{\frac{1}{2}}$ and $M\beta$ proportional to one another; and in the light of what we have just found for the free metals, we ought to compare the square of the part F carried by a metal atom into $(M^2l)^{\frac{1}{2}}$ in compounds with the part B carried into M/ρ. Here are the values for the Li family:—

Table XXXI.

(Li family in compounds.)

	Li.	Na.	K.	Rb.	Cs.
B or volume of atom ...	2·0	7·4	18·6	34·4	56·0
F^2	5·8	12·2	21·2	36·0	53·2
$\cdot 9B+4\cdot 4$	6·2	11·1	21·1	35·4	54·8

The first two rows of numbers show that F^2 and the volumes of the atoms in compounds run a parallel course, but are not strictly proportional to one another as in the free state, yet the numbers in the third row show that the connexion between the two quantities in the combined state is the simple one

$$F^2 = \cdot 9B + 4\cdot 4,$$

while for the free atoms the relation was

$$M^2 l = \frac{1}{2\cdot 7} \frac{M}{\rho}.$$

In the Be family we get

Table XXXI. (*continued*).

(Be family in compounds.)

	Be.	Mg.	Ca.	Sr.	Ba.
B	1·0	5·6	8·6	10·6	16·6
$F^2/4$	4·4	7·3	10·2	13·7	17·6
·9B+3·0	3·9	8·0	10·7	12·5	18·0

The data of this family are affected with considerable uncertainty, but the third row of numbers shows that probably in compounds

$$F^2/4 = \cdot 9B + 3\cdot 0,$$

while for the free metals the relation was found to be

$$M^2 l = M/\rho.$$

It is noticeable that the constant ·9 for the Be family is the same as that for the Li family.

It is not possible with the existing data to follow this interesting inquiry into the other metallic families, and trace the transition from the form of relation $F^2 = aM/\rho + b$ holding amongst the powerfully positive metals to the form $F = cM\beta$ (c being a constant) characteristic of the non-metals, and apparently of some weakly electropositive metals.

We proceed now to the surface-tension method of finding $M^2 l$ for the metals, chiefly to draw attention again to a discrepancy between the values of $M^2 l$ for the free metals given by the Kinetic Theory of Solids and those by the method of surface-tension. This was pointed out at the end of the paper on the Kinetic Theory of Solids, but it can be brought out here in a more definite manner and with more interest, seeing that the two methods have been proved in this paper to give accordant results for binary compounds. To the gain of the Kinetic Theory of Solids, the discrepancy will be largely cleared up as due to molecular complexity.

The equation for the surface-tension of the elements has to be modified from the form in which it was used for compounds, because in the Laws of Molecular Force (Phil. Mag. March 1893) it was shown that the virial constant l of compounds falls in the liquid to half of the limiting value in the gas, whereas in the elements H_2, O_2, and N_2 it retains the same value in both states. Now the equation (9) was designed to give the value of l for compounds in the gaseous state from measurements of their surface-tensions as liquids, therefore in applying equation (2) to the elements we must provisionally divide by 2, and get

$$M^2 l = \frac{9346}{2} \times 10^{-6} \alpha_m (M/\rho_m)^{\frac{2}{3}}, \quad . \quad . \quad . \quad (19)$$

in which M will be taken as the usual atomic weight. The following are the data for the metals and a few other elements given by Quincke (Pogg. *Ann.* cxxxv. & cxxxviii.), with the values of $M^2 l$ calculated from them by the last equation, also the values of $M^2 l$ reproduced from Table XXIX. as given by the Kinetic Theory of Solids, and finally the ratio of the two values of $M^2 l$.

Table XXXII.

	Na.	K.	Cu.	Ag.	Ag.	Au.	Au.
α_m	26	37	59	43	80	100	131
ρ_m	·97	·86	8·2	10·0	10·0	17	17
M/ρ_0	23·7	45·4	7·2	10·2	10·2	10·2	10·2
$M^2 l$	23·7	98	8·2	10·4	19·5	27·1	35·6
$M^2 l$ from Ta. XXIX....	8·6	16·2	11·1	15·9	15·9	18·7	18·7
Ratio	2·7	6·0	·8	·7	1·2	1·4	1·9

	Zn.	Zn.	Cd.	Hg.	Sn.	Pb.	Pb.
α_m	88	83	71	59	60	46	34
ρ_m	6·9	6·9	8·4	13·6	7·1	11·0	11·0
M/ρ_0	9·1	9·1	12·9	14·7	16·1	18·1	18·1
$M^2 l$	17·3	16·3	24·8	24·3	29·6	28·8	21·3
$M^2 l$ from Ta. XXIX....	7·3	7·3	9·7	4·8	10·9	15·3	15·3
Ratio	2·4	2·2	2·5	5·0	2·7	1·9	1·4

	Sb.	Bi.	Fe.	Pd.	Pt.
α_m	25	39	26	136	169
ρ_m	6·5	9·7	7·5	10·8	18·9
M/ρ_0	17·9	21·1	7·2	9·2	9·1
$M^2 l$	14·8	30·1	13·3	28·8	38·1
$M^2 l$ from Ta. XXIX.	16·4	16·1	16·9	20·6	26·1
Ratio	·9	1·9	·8	1·4	1·4

Table XXXII. (*continued*).

	S.	Se.	P.	Br.
a_m	4·2	7·2	4·2	6·3
ρ_m	1·97	4·2	1·83	3·25
M/ρ_0	15·7	17·1	13·5	27
M^2l........................	2·1	4·5	2·2	6·2
M^2l from Ta. XXIX. .	6·3	10·0	4·4	7·0
Ratio	·33	·45	·50	·88

Where two values of a_m are given for one metal, they are the result of different methods of measurement; the data are all Quincke's except one of the measurements for lead made by myself. If matters were exactly as we suppose them to be, in applying equations (9) and (19) the values of the ratio in the last table ought to be 1, or a constant near to 1, such as we found in the case of the binary compounds, while the range in the actual values of the ratio is from ·33 for S to 6·0 for K. In seeking for the reason for this discrepancy, we must remember that in using the equation (19) of the capillary method we have assumed that the characteristic equation of the metals is on the same type as that of the element gases; but there is this distinction between the metals and the element gases, that some of the metals, namely Na, K, Zn, Cd, and Hg, are known to be monatomic in the vaporous state, while the element gases are diatomic; and it is exactly for these metals and tin that the ratio in the last table has its largest values, while the smallest values belong to S, Se, and P; and S and P are well-known instances of exceptional molecular complexity, their vapour-densities at low temperatures being such as correspond to the formulas S_6 and P_4. It is therefore probable that the discrepancy has to do with an effect of molecular complexity not taken account of in equation (19). We saw that the distinction between the diatomic element gases and compounds was expressed by introducing the factor 2 into the left side of equation (2); and if we suppose that amongst the elements the effect of molecular complexity is to introduce into the right side of the equation (19), namely

$$M^2l = \frac{9346}{2} \times 10^{-6} a_m (M/\rho_m)^{\frac{1}{3}} ,$$

a factor equal to the molecular complexity, defining the molecular complexity of an element as the number of pairs of atoms in its molecule, which is 1/2 for Na, K, Zn, Cd, and Hg, 2 for P, and 3 for S, then the values of M^2l by the capillary method in the last table would be multiplied by these factors, and also the values of the ratio. Treating the molecular complexity where unknown as 1, then the values of the ratio become:—

Na.	K.	Cu.	Ag.	Ag.	Au.	Au.	Zn.	Zn.	Cd.	Hg.	Sn.
1·3	3·0	·8	·7	1·2	1·4	1·9	1·2	1·1	1·2	2·5	2·7

Pb.	Pb.	Sb.	Bi.	Fe.	Pd.	Pt.	S.	Se.	P.	Br.
1·9	1·4	·9	1·9	·8	1·4	1·4	1·0	·9 ?	1·0	·9

The numbers for K, Hg, and Sn are about double the average for the other elements; the experimental value of α_m is said by Quincke to be uncertain in the case of K, and also for Cu and Fe, while the pairs of values given for Ag, Au, and Pb show that in some cases a large experimental error is possible in these difficult measurements. Thus the effect which we have assumed as due to molecular complexity brings the discrepancies within the range of experimental error in all the satisfactory cases except that of Hg. But even if the explanation just suggested for the inequalities amongst the values of the ratio in the last table proves not to be correct, it has at least been demonstrated that these inequalities do not indicate any real discrepancy amongst our equations, because the effect of different molecular complexity has to be allowed for. Thus while the results of the capillary method of finding M^2l do not, in the case of the elements, confirm the values given by the Kinetic Theory of Solids, they do not invalidate them, and the complete explanation of the relation of the two sets of values may not be obtainable till we know the characteristic equations of the metals.

The transition cases from metal element to non-metal element will not be gone into at present, but it will be advantageous to gather here the values of $M\beta$ and $(M^2l)^{\frac{1}{2}}$ and their ratio for the non-metal elements. We have seen reasons for believing the values in Table XXIX. to be relatively correct on the whole, although it must be expected in such an instance as that of Cl that the method there used for finding M^2l must give a rather rough value: in the following table the values given are reproduced from Tables VIII. and XXIX.

TABLE XXXIII.

From Table VIII.

	H_2.	O_2.	N_2.	Cl_2.
$M\beta$	8·6	19·3	22·7	34
$(M^2l)^{\frac{1}{2}}$	0·47	1·08	1·11	2·4
Ratio	18	18	20	14

Table XXXIII. (*continued*).

From Table XXIX.

	Cl.	Br.	I.	S.	Se.	P.
$M\beta$	17	22	25·6	15·7	17·1	13·5
(M^2l)	1·9	2·6	3·6	2·5	3·2	2·1
Ratio	9 0	8·3	7·1	6·3	5·3	6·4

As has already been pointed out, the numbers for Cl are rough, so that no importance attaches to the discrepance between the ratio 9 for Cl and 14 for Cl_2, which numbers ought to be identical. All that the table shows is that the relation found to hold between $M\beta$ and $(M^2l)^{\frac{1}{2}}$ in the gaseous non-metals does not extend to the other non-metals. The transition cases from metal to non-metal will have to be worked out before the principle ruling in the values of $(M^2l)^{\frac{1}{2}}$ for the non-metals becomes clear.

4. *General Summary and Analysis of Molecular into Atomic Attractions.*

The chief result of the present inquiry has been the demonstration that M^2l, which occurs in the treatment of the attractions of like molecules, and which represents Am^2 in the expression $3Am^2/r^4$ for the attraction between two molecules of mass m, can be analysed into two factors $(M^2l)^{\frac{1}{2}}$ which are the sum of numbers characteristic of the atoms composing the molecule whose mass referred to the atom of hydrogen is M. This is the logical outcome of the proof given in the papers on "The Attraction of Unlike Molecules," that the attraction of two unlike molecules is expressed by the product of two parameters characteristic of each and equal to the square roots of the corresponding attractions for a pair of each of the molecules. The values of $(M^2l)^{\frac{1}{2}}$ studied in this paper are therefore relative values of $A^{\frac{1}{2}}m$. But as we have found no evidence of a direct connexion between m and $A^{\frac{1}{2}}m$, it is desirable to remove all implication of such a connexion, which was originally adopted for the sake of analogy with the Newtonian law of gravitation. Accordingly $A^{\frac{1}{2}}m$ would be better denoted by a single symbol a, so that the attraction between two molecules of mass m_1 at distance r apart is $3a_1^2/r^4$, and of two molecules of masses m_1, m_2 is $3a_1\,a_2/r^4$, and so on.

The fact that a for a molecule is the sum of parts due to the atoms in it enables us to analyse molecular into atomic attraction; for if two molecules of composition B_b, C_c, D_d...

are at a distance r apart, and if the force between the atom or radical B in one molecule and C in the other is $k\beta\gamma f(r)$, and between C in one and D in another is $k\gamma\delta f(r)$, and so on, then the attraction between the two molecules is

$$k(b^2\beta^2+c^2\gamma^2+\ldots+2cd\gamma\delta+2db\delta\beta+2bc\beta\gamma+\ldots)$$
$$=k(b\beta+c\gamma+d\delta+\ldots)^2,$$

so that a, the parameter for the whole molecule, is given by

$$a=k^{\frac{1}{2}}(b\beta+c\gamma+d\delta+\ldots),$$

which is the symbolical statement of our result for the carbon series of compounds that the parameter a for a molecule is the sum of parts due to the separate atoms and radicals in it, and shows that in these compounds the atoms and radicals attract one another with a force proportional to the product of parameters characteristic of each. This does not imply that the parameter belonging to an atom is invariable, for the atoms in a free element have different parameters from those they possess in a compound: by chemical combination both the volumes and force-parameters of many atoms are altered, and the amount of alteration depends on the chemical function of the atom in the molecule; while the chemical function of an atom or radical in an organic compound is constant, its force-parameter is constant. This influence of chemical function on the parameter of molecular force becomes manifest in the typical inorganic compounds, especially of the metals. If the compound is of the type RS_n, where R is an atom of valency n combined with n monad atoms S, then the expression for a takes the form

$$a=\left(\frac{k}{n}\right)^{\frac{1}{2}}(\rho+n\sigma)$$

(ρ and σ being parameters belonging to R and S); or perhaps a more suggestive form in which to put it is

$$a^2/n=(\rho/n+\sigma)^2,$$

which means that the mutual energy of two molecules of this type divided by the number of equivalents in each can be obtained by regarding each equivalent as a separate attracting entity. The equations just given hold true not only when R is a metal and S a non-metal, but also when R is an acid radical of any basicity and S a monad metal. The law for the more general case of a compound R_mS_n has not been investigated in this paper because of the want of suitable data; nor have the transition cases between the simple typical compounds and the organic series been worked out. It is interesting to find in molecular force a new clue towards the realization of the desire of chemists to trace out the transition from the dualistic to the unitary type of compound.

The atomic parameters $\beta, \gamma, \ldots \rho, \sigma \ldots$, relative values of which have been given under the symbol F, which is the part contributed by an atom to $(M^2l)^{\frac{1}{2}}$, have been shown to be related to the volumes of the atoms; in the organic compounds many atoms and radicals have F closely proportional to the volume of the atom, and in the case of the halogens this holds good also in the inorganic compounds. Denoting the volume of an atom by B, the approximate relation is $B=10\,F$ or $9\,F$, but for a compound acid radical of basicity higher than one the relation becomes $B=9F/2$; here again is evidence of chemical influence on molecular force. In the case of metallic atoms in their compounds, it has been shown that F is not proportional to the volume of the atom, and on passing on to the uncombined metals it is found that F, which represents the atomic parameter, is in the main families of metals approximately proportional both to the square root of the volume of the atom and the square root of the valency, and in the subfamilies is a simple multiple of a number which is so proportional. On returning to the metal atoms in the combined state, it was found that the relation is $F^2=aB+b$ in each family, a and b being constants characteristic of the family. The profound influence of valency in the uncombined metals is again of deep chemical interest, as is also the great difference in the law connecting atomic parameter and volume from that holding amongst the extreme non-metals. These are the main results; amongst subsidiary results may be mentioned a certain amount of confirmation given to the Kinetic Theory of Solids by its successful application to the calculation of force parameters, successful insomuch as its results are in harmony with those obtained by a perfectly independent method. This confirmation is the more useful because it applies to the extension of the theory to compound solids, whereas in the original paper the metals only were treated of.

Melbourne, August 1894.

II. *The Influence of Temperature on the Specific Heat of Aniline.* *By* E. H. Griffiths, *M.A.*[*]

[Plates I. & II.]

OUR knowledge of the effect of changes of temperature upon the specific heat of substances is limited. The reason of this is evident, for, in addition to the difficulties of thermometry, the experimental methods usually adopted are based on comparisons in which water is used as a standard, and our knowledge of its capacity for heat at different temperatures is far from satisfactory. The conclusions of Rowland (1879), of Bartoli and Stracciati (1893), and my own investigation completed in 1892, all point to the fact that the specific heat of water diminishes as the temperature rises to 20° C., at which temperature Bartoli and Stracciati find it is a minimum. My observations did not extend beyond 27° C., up to which temperature I found no signs of a minimum, which Rowland places at about 34° C. When such discrepancies exist with regard to the standard, it is not surprising that the conclusions arrived at regarding other substances are unsatisfactory.

For other reasons water is by no means an ideal standard for calorimetry. Its capacity for heat is so great that the changes in temperature caused by the immersion in it of bodies whose specific heats are small are too minute to be measured with exactness under ordinary circumstances. The difficulty is surmounted in practice by causing the immersed body to cool through a considerable range. Other errors are, however, introduced by this method, for the transference of the hot body into the cool water can rarely be conducted without loss of heat. What we require is a liquid of small capacity for heat whose temperature-coefficient of specific heat is accurately known. It should also, if possible, be a liquid easily obtainable in a fairly pure state and should have a low vapour-pressure at ordinary temperatures. I believe that in Aniline we possess such a liquid, and I hope to be able to adduce sufficient evidence to lead to the conclusion that its specific heat is now known with considerable accuracy over a range of 15° to 52° C.

The method I have adopted is an old one, viz. a supply of heat to the interior of the calorimeter by means of an immersed conductor whose ends are kept at a constant potential-difference. I admit that there are difficulties inseparable from the method (such as doubts as to the actual resistance of the conductor when its temperature is raised by the current, &c.), but when once these difficulties are overcome, there is no such accurate means of determining the quantity of heat passed into a calorimeter in a given time.

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[*] Communicated by the Physical Society: read October 26, 1894.

The limits of this paper forbid any detailed account of the somewhat complicated apparatus used in this investigation, and I do not contend that it is of the form which I should have selected had my object simply been to determine the specific heat of aniline. I am at present engaged in a determination of the latent heat of evaporation of water and other liquids at different temperatures, consequently the apparatus has been designed and put together in anticipation only of that investigation, and many portions of it are unnecessary and in fact detrimental to the inquiry I am now describing. Hence I have been compelled to adopt methods of observation which may not, at first sight, seem the most advantageous.

I have in my possession an apparatus for maintaining the walls of a chamber at a constant temperature. The arrangement has been fully described in a communication entitled "The Mechanical Equivalent of Heat," Phil. Trans. clxxxiv. A (1893), and as I shall somewhat frequently have to refer to this paper, I will now label it with the letter "J." Briefly, the apparatus as there described consists of a tank containing about 20 gallons of water within which is a steel chamber shaped somewhat like a hat-box with vertical sides, the space between the double walls and floor containing rather more than 70 lbs. of mercury, which communicates by a narrow tube with a gas-regulator differing but little from the ordinary pattern. Thus a row of about 50 tiny gas-jets (placed under a tube through which water is always flowing) are so controlled as to be distinctly affected by a change of $\frac{1}{400}$° C. in the temperature of the steel chamber. An addition has been made to the apparatus since the publication of the description in paper J, where it is stated that tap-water continually passed into the tank through a silver tube placed above the gas-jets: this plan answered admirably from the temperature of the tap-water (10° to 12° C.) to about 30° C. Last year, however, Prof. Callendar and I wished to use the tank for purposes of comparison of platinum and air thermometers up to 50° or 60° C., when it was found that alterations in temperature presented themselves, occasionally amounting to as much as $\frac{1}{50}$° C.,—the lag in the temperature of the large mass of mercury being so great that when the gas was lowered by the action of the regulator, the resulting inflow of cold water tended to lower the temperature of the tank before the reaction of the regulator could again heat the inflow. As now arranged, when working above temperatures about 20° C. a small motor acts as a heart and, the tap-water being shut off, pumps the tank-water itself round through the silver tube placed above the gas-jets. The water, by passing through the pump &c., is slightly cooled: thus the work of the regulator is confined to simply supplying the heat lost by convection, radiation, &c., and it performs this task admirably. As an illustration, I may mention that in the series of over 50 experiments treated of in this communication on only one occasion did the temperature of the steel chamber change by as much as $\frac{1}{100}$° C. throughout the duration of an experiment. On the solitary occasion that a change amounting to nearly $\frac{1}{50}$° C. was observed, the cause was found in the caking of the lime through which the gas was passed on its way to the regulator, and, in consequence, the experiment was discarded before working out its results.

A large screw, placed in the tank-water, revolved at about 800 times per minute and raised a considerable sea—the flow passing round, under, and over the steel chamber, the top of which was about 4 in. beneath the surface of the water.

The calorimeter was formed of brass and was suspended by glass tubes which, after passing through the lid of the steel chamber and through the water, projected above the lid of the tank. The diameter and depth were each about 10 centims. and the capacity about 700 cubic centims. Within it was suspended a silver flask with which three silver tubes communicated. One was connected with a glass tube passing to the exterior through which substances could be introduced. The second tube, which was about 18 feet in length, was, after leaving the top of the flask, twisted into a spiral within the calorimeter; the other end, terminating in the lid of the calorimeter, was then connected by a glass tube with a four-way tap entirely immersed in the outer tank. The third tube, which opened into the bottom of the flask, communicated with about 30 feet of copper tubing placed in the tank-water. The object of the whole arrangement was that the gas on leaving the calorimeter (after evaporating any liquid in the flask) should have acquired the temperature of the calorimeter, and that any gas passed into the flask should assume the temperature of the outer tank. True, this portion of the apparatus was not necessary to the experiments on aniline, but I have felt it advisable to describe it, as explaining some of the subsequent operations.

A coil of fine german-silver wire, supported on glass pillars, was placed within the calorimeter and so arranged as to surround the silver flask. Communicating with this coil were four leads—Nos. 1 and 2 of which were fastened to one end, and Nos. 3 and 4 to the other end of the coil at the roof of the calorimeter, and, passing up through the steel vessel, communicated with the exterior. Nos. 1 and 3 formed the ends of a circuit in which were placed a high-resistance galvanometer and the Clark cells; Nos. 2 and 4 a circuit which contained a rheochord of special construction (for a description see paper J), reversing-keys, and storage-cells. It was thus possible to maintain the ends of the calorimeter-coil at a difference of potential equal to that of any number of Clark cells; and I am convinced that the variations in the potential-difference during the course of an experiment rarely amounted to $\frac{E}{10,000}$. (The grounds on which this somewhat bold statement is based are fully given in paper J, p. 283.) The contents of the calorimeter could thus be heated or cooled without any disturbing effects from external causes. By means of the electrical arrangements above described, the supply of heat could be regulated at will and accurately determined, while, by the insertion into the flask of a volatile liquid such as ether, it was possible, by adjusting the current of dried air, to regulate the rate of cooling.

Particulars of the Clark cells have already been published (paper J, pp. 286–288), and the whole 36 maintain to-day almost exactly the same relative values as they had when compared with the Cavendish standard in 1892: there is, therefore, every reason to believe that their absolute value remains unchanged. I have not yet had time to repeat the comparison with the Cavendish standard, but I hope to do so shortly. I do not, however, anticipate that any correction will be found necessary. The whole of these cells were contained in a bath, through which the tap-water was turned by means of a regulator whenever the temperature exceeded 15° C.

The calorimeter previously described differed considerably from that used in my determinations of the mechanical equivalent. During these experiments the air-pressure in the space between the walls of the calorimeter and those of the steel chamber containing it was reduced to from ·5 to ·2 millim. as measured by McLeod's gauge; and my observations proved that there was a strangely rapid diminution in the loss by convection, &c., when the pressure fell below half a millimetre*. I proposed, however, during the experiments for which this second calorimeter was designed to maintain the calorimeter and the steel chamber at nearly equal temperatures, and it did not, therefore, appear so necessary to guard against convection and radiation gains and losses. Previous experience had convinced me of the absolute necessity for keeping this intramural space dry, for I found that the slightest moisture in the contained air has the most astonishing effect in changing the conditions. It was therefore necessary that all joins should be absolutely tight, for the lid of the steel chamber was under water, and I proposed, in the preliminary experiments, to place water within the calorimeter. The use of indiarubber was forbidden, as I intended to insert ether in the silver flask and aniline in the calorimeter; and even if such had not been the case, indiarubber connexions are, at the best, unsatisfactory and unreliable. I decided, therefore, not to commence my experiments until I found that the apparatus was absolutely gas-tight in all parts; and I may mention that the greater part of last summer was unsuccessfully devoted to the endeavour to secure perfection in this respect. During last winter I spent considerable time in the effort to obtain some suitable medium by which to join glass to metal; and with the assistance of Mr. Thomas I was at last successful in procuring an alloy by which an air-tight join could be formed*, and which would stand considerable changes of temperature. Five glass tubes passed from the calorimeter to the steel lid, rendering ten such glass-to-metal joins necessary, besides several similar ones in the exterior connexions.

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* A similar conclusion was arrived at by Bottomley; see Phil. Trans. 1887, A.

In the spring of this year the intramural space was exhausted until the reading of the McLeod gauge connected therewith was reduced to 11, indicating a pressure of about 0·12 millim. The apparatus was then left untouched for a month except that the temperature was occasionally raised or lowered, and at the end of that time the reading of the gauge was still less than 12. Dry air was then readmitted to this space, and the silver flask with its connected tubes (embracing about 50 feet of tubing with several joins) tested in a similar manner. Those who have had to deal with low pressures will understand that when all was found satisfactory a great difficulty had been surmounted. I did not retain this vacuum during the experiments, as I felt that it would subject the glass tubes &c. to a continuous strain which the conditions of the experiments rendered unnecessary. The labour had not been lost, however, for I was able to count with confidence on the gas-tightness of the whole apparatus.

I now pass to a description of that vital part of any such investigation, viz. the thermometry. The method I proposed to adopt necessitated extremely accurate measurements of small differences of temperature. The actual elevation was of little consequence, and therefore the use of differential thermometers immediately suggested itself. Two platinum thermometers (labelled AB and CD) were constructed with great care: four stout platinum leads passed down the stem of each, supported and insulated in the usual manner by small disks of mica, and the resistance of all these leads was made as equal as possible before attaching the coils. Great attention was given to this matter, and it is safe to assume that the leads in no case differed amongst themselves by 1 in 10,000. The coils, consisting of a particularly pure sample of platinum wire, were then attached, and several days were devoted to securing their equality. Their resistance in ice was about 18 ohms: thus $\frac{1}{1800}$ of their resistance could be directly determined in the box. The galvanometer swing was about 500 for a change of ·01 in the box; and such equality was secured that when both thermometers were placed in ice (the necessary precautions being taken with regard to exterior connexions &c.), no difference in the swing of the galvanometer could be observed; thus they differed by a quantity certainly less than 1 in 100,000. This equality, although not a necessity, was a great convenience.

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* Proc. Camb. Phil. Soc. 1894.

Although cut from the same length of wire and insulated in a precisely similar manner, the coils did not possess exactly the same coefficients. The resistances in steam and sulphur were repeatedly determined and checked by observations in the vapour of aniline. Both thermometers were on several occasions heated to a red heat, the hard glass tubes containing them becoming slightly bent in the process; but since this annealing no further change has been observable in them. The method of completely standardizing such instruments has been fully described by Professor Callendar and myself in Phil. Trans. 1891, A, and I need not therefore here dwell upon it. The values of δ differed slightly, viz. 1·513 and 1·511; but such a difference, even if not allowed for, would over the range 0° to 100° C. in no case cause an error exceeding about $\frac{1}{2000}$° C. in elevation. These thermometers were so connected that the compensating leads of A were placed in series with the coil of B, and *vice versâ*. Any heating of the stem of A or B, therefore, added an equal resistance to each arm of the bridge; and as the leads were everywhere bound together, the indications were absolutely independent of all changes in temperature except those of the bulbs.

Great care is required to accurately determine the fixed points of such thermometers. For example, a difference of 1° at 100° C. made a difference of ·067835 ohm: thus a difference of 1 millim. on the barometer caused a difference of ·00244 ohm. Readings of the pressure were taken on a standardized $\frac{3}{4}$-inch diameter mercury-barometer, and also on a compensated sulphuric barometer suspended beside it. It was found that the observations, if corrected to 100° C. by the pressure as deduced from a mercury-barometer, were not in close agreement; but if by the sulphuric-acid barometer, the results were satisfactory. On examination it appeared that the first observations of each series, when corrected for pressure, were in harmony whichever barometer was used; but such was not the case with subsequent ones of the same series. The cause is, I believe, to be found in the necessary handling of the barometer that takes place when adjusting the mercury to the ivory point. The temperature within the case undergoes a change, and the indications of the thermometer usually placed within the metal tube surrounding the barometer give but little information as to the real temperature of the mercury column, whereas the sulphuric-acid barometer requires no manipulation and is independent of such temperature changes. As an example of the consistency of the boiling-point when corrected by the H_2SO_4 barometer, I give the following *consecutive* results:—

(Difference in R for 1° C. at 100° = ·067835.)

Date.	R after correction for temperature of box, plug errors, &c.	Barometer corrected to sea-level, lat. 45° and temp. 0° C.	Boiling-point.	Correction to 100° C.	R_1 (at 100° C.).
Thermometer AB.					
June 3 ...	24·58798	761·10	100·040	−·00271	24·58527
„ 5 ...	24·57187	754·67	99·802	+·01342	24·58529
July 7 ...	24·58336	759·25	99·972	+·00190	24·58526
Thermometer CD.					
June 3 ...	24·58606	761·10	100·040	−·00271	24·58335
„ 5 ...	24·56961	754·52	99·796	+·01383	24·58344
July 7 ...	24·58163	759·34	99·975	+·00168	24·58333

The above examples will show that it is possible to determine the resistance at 100° C. to better than 1 part in 250,000, and nearly the same order of accuracy is obtainable, with proper precautions, in the vapour of sulphur.

I believe the most difficult point to accurately determine is freezing-point, and for really satisfactory determinations it is advisable to use distilled-water ice; but if this is manufactured in the usual manner there is great danger that some trace of salt may be carried from the freezing-mixture to the ice. One precaution I have found advantageous when using ordinary ice, viz., on adding water to the powdered ice it is advisable to use water resulting from the melting of that ice itself rather than either distilled or tap water.

I will not burden this paper with any further detailed account of the standardization of these thermometers. Between March 4th and July 7th the fixed points were determined on over 30 occasions, in ice, steam, or sulphur vapour, and no variation which would affect temperature measurements between 0° and 100° C. by as much as $\frac{1}{2000}$° C. presented itself during the latter half of these observations, the record and reductions of which alone make a large pile of manuscript.

The two thermometers, with their leads connected as described, were placed at opposite ends of a bridge wire of platinum-silver. During the spring of this year this wire was subjected to a most careful calibration by what was practically Carey Foster's method, and it proved to be more unequal than I had expected. It was therefore re-calibrated by a different method in which a resistance-box was used as a shunt, and the agreement between the results was satisfactory. The whole wire was 80 centim. long and had a total resistance of about ·4 ohm. For convenience, and to avoid thermal effects, a similar wire connected with the galvanometer was laid alongside it, and the sliding-piece was fitted with a screw so arranged that a small turn of the screw-head made contact with both wires*.

The wire and contact-maker were covered by a thick copper shield (the screw-head projecting through a narrow slit) passing from end to end of the bridge: thus the temperature of the wire was kept uniform. By means of a vernier the divisions on the scale could be read to $\frac{1}{10}$ millim., which with this wire and thermometers AB and CD indicated at 50° C. a temperature difference of ·000915° C.† The temperature-coefficient of this wire was found to be ·00029. The resistances of the different parts of the wire were, after correction for the errors of individual coils, &c., merely expressed in terms of the mean box ohm, the absolute value being of no consequence so long as the fixed points were determined in terms of the same standard. The remaining two arms of the bridge were constructed of german-silver. They were wound together, boiled in paraffin, placed in a bottle, and I expended much care in finally adjusting them until equal. Their resistance was about 5 ohms and the galvanometer about 8 ohms, which, assuming the resistance of the thermometers as about 20 ohms each, would give nearly the maximum of sensitiveness. A single storage-cell was always used, and a resistance of 40 ohms was placed in the battery circuit when the thermometers were in ice. A table was then calculated which gave the resistance necessary in the battery circuit when the thermometers were at any temperature in order that C^2R (where R is the thermometer resistance) should be constant. Thus the rise in the temperature of the thermometer coils due to current-heating was always the same, and consequent errors were eliminated, a point to which I attach considerable importance.

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* This method of making the connexion is due to Professor Callendar, and is exceedingly effective and convenient.

† A thicker wire giving a more open scale was tried at first, but found to be less convenient than the one finally adopted and calibrated.

The value of $R_1 - R_0$ in thermometer AB was 6·88815; therefore a difference of 1 ohm at 50° C. indicated a difference of 14°·5177 C., and as

$$\frac{d\,pt}{dt} = \left\{ 1 - \delta\,\frac{2t - 100}{100^2} \right\}^{*},$$

the degree value of any bridge-reading at other temperatures can be deduced.

There was no difficulty, in the arrangement above described, in reading with certainty a difference of $\frac{1}{1000}$° C., and, as an illustration, I may mention the fact that if the thermometers were placed in separate hypsometers side by side on the bench and one of the hypsometers was then removed to the ground (about 3 feet below), the difference in the bridge-wire reading thus caused slightly exceeded ·4 millim.

Before leaving this portion of the subject I may mention that I carefully compared the thermometer AB with two standards from the International Bureau of Weights and Measures, which passed through my hands this summer on their way to Sydney University, and further with a separate standard sent me by the Bureau in February 1893. As the particulars of this comparison are now in the press†, I

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[*] Trans. 1891, A. p. 142.

[†] 'Science Progress,' September 1894.

need not refer to them further than to say that the results were most satisfactory.

When the experiments were in progress the thermometer CD was placed in a hole drilled in the wall of the steel chamber parallel to the side and separated from the inner surface by only $\frac{1}{16}$ in.: thus it assumed the temperature of the walls surrounding the calorimeter. Thermometer AB passed within the calorimeter and was immersed to an inch above its bulb in the contained liquid. The reading on the bridge-wire thus gave the difference between the temperature of the calorimeter and the walls of the surrounding chamber.

To ascertain the actual temperature and the *constancy* of the temperature of the surrounding walls, a second hole, like that already described, was drilled in the steel, in which a mercury thermometer of open scale was placed. The stem, where it protruded above the lid of the tank, was surrounded by a glass tube up which the motor pumped the tank-water, which, passing out at the top, returned to the tank. The stem, therefore, was maintained at a steady temperature, and the fluctuations observed might be considered as solely due to changes in the walls of the steel chamber. The stem of thermometer A (used at the lower temperatures) was divided into millimetres, about 27 to a degree, and No. II. (used at the higher) about 20 millim. per degree. They were observed through a telescope containing a micrometer-scale giving direct readings to $\frac{1}{10}$ of a millimetre. The tenth of one of these divisions could be estimated, and thus changes of $\frac{1}{1000}$° C. (*i.e.* about ·025 millim.) were easily observable. This was important, as the bridge-wire readings had to be corrected for any movement in the temperature of thermometer CD—that is, the temperature of the walls of the chamber.

The stirrer (which consisted of two nearly vertical narrow paddles, reaching from top to bottom of the calorimeter) was so placed as to throw the liquid across the silver flask and coil against the thermometer. This form of stirrer was not the one I should have adopted had the apparatus been designed solely for the experiments which I am now describing. In that case I should have preferred the form described in paper J, which threw the liquid from the bottom to the top of the calorimeter; and I believe that such irregularities as have presented themselves in these experiments, especially with the smallest mass, are due to insufficient stirring. When the calorimeter is full of liquid the nature of the stirring is of less consequence; and as I proposed in the experiments for which the apparatus was designed to completely fill the calorimeter, I adopted the form which it appeared to me would generate the least heat compatible with efficient mixing. The stirrer was supported in the same manner as that described in a former paper; that is, its bearings were entirely external to the calorimeter except at the base, where, to check vibration, an agate cylinder hung within a ring *.

In place of the 2000 revolutions per minute used in my former work I confined myself, for the reasons above stated, to a comparatively slow rotation of from 500 to 300 revolutions per minute. The revolving shaft was electrically connected with the chronograph in such a manner that the time of every 1000 revolutions was automatically recorded on the tape.

Before commencing the observations on aniline I introduced 299·35 grms. (*in vacuo*) of water into the calorimeter, and, with a view to ascertaining the water-equivalent, performed a few experiments to determine the rate of rise when a known current was passed through the coil. The point was not of great importance, as I proposed to determine the specific heat of aniline by a method requiring no knowledge of the water-equivalent, which, however, when the specific heat of aniline was known, could be deduced from the experiments, and thus a previous determination by means of water would serve as an independent test of the accuracy of the results. I had not covered the german-silver coil with any insulator, since, aniline being itself an insulator, the precaution was unnecessary; and this freedom to use the naked wire was one of the chief reasons which led to the adoption of aniline as a suitable liquid for my subsequent work. I was therefore aware that I could not expect very satisfactory results from the use of water. The polarization was considerable, as shown by the back E.M.F. at the termination of an experiment, and also by the difficulty experienced in making any accurate determination of the coil-resistance. However, it was subsequently found that the experiments gave very fair results. The temperature was raised from about ·5° C. below to ·5° C. above the surrounding temperature (*i. e.*, through about 12 centim. of the bridge-wire), and the times of passing the several divisions of the bridge-wire were recorded on the chronograph. Five experiments were performed, and the results of the first three gave a water-equivalent of 80·1, and Nos. 4 and 5 of 79·8. They were thus divided into groups before the results were calculated, as the coil showed decided signs of change in resistance between the two batches of experiments. I had proposed to continue these experiments with a different mass of water, but became alarmed as to the effect on the coil of the change that was going on, and decided to withdraw the water, for had the coil become useless from any cause, the whole apparatus would have had to be taken to pieces and the base of the calorimeter unsoldered, &c., involving a delay of at least a week or two.

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* A portion of the shaft of the stirrer was constructed of ivory, to diminish its thermal conductivity.

During the time that the water was in the calorimeter I performed a considerable number of experiments to determine the rise in temperature due to the work done by the stirrer. With this form of stirrer and the low rates, tr^2 was practically a constant, where t was the time of rising 1 centim. of the bridge-wire and r the rate of revolution per second. The resulting correction was comparatively small, amounting to about $\frac{1}{25}$ of the heat generated by the current during the water-equivalent experiments; thus any small error in the correction introduced when eliminating the heat supplied by the stirrer became unimportant.

After the water was withdrawn, the whole apparatus was kept for three days at a temperature between 40° and 50° C., while dried air was forced continuously through every part of it. At the end of this time a sulphuric-acid bulb (through which the air passed on its exit from the apparatus) showed no increase in weight. I then introduced 294·99 grms. (*in vacuo*) of aniline into the calorimeter *.

I will at once state that no great pains were taken to secure an absolutely pure specimen of aniline. For my subsequent experiments the purity of the aniline was a matter of no consequence, as I only required to know the actual capacity of the calorimeter and contents at different temperatures.

Again, as regards the purposes of this investigation I think that it will be of greater service if I am able to supply experimenters with the specific heat of a quality of aniline at all times procurable, rather than if I gave the constants of a quality only to be obtained with difficulty. The sample I used was supplied by Messrs. Harrington Bros., as "pure colourless," and had but a light brown tinge. It was redistilled by me once before use, and I also determined its boiling-point, which was in agreement with that of a specially pure sample which I had examined on a previous occasion †. Further (and this I have always found to be a fair test of the purity), the temperature of the boiling-point did not change during distillation.

From the time that aniline was first introduced into the

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[*] The precautions observed in order that the mass introduced might be accurately determined are fully described in paper J, p. 418.

[†] Trans. 1891 A, p. 64.

calorimeter all signs of polarization disappeared, and the insulation of the coil was very perfect.

I will now describe the method of conducting an experiment.

The tank was first brought to the desired temperature, and the experiment was not proceeded with until the tank-temperature had had time to become steady. Freshly distilled ether was then introduced into the silver flask, and dried air passed through it (the stirrer in the surrounding aniline being continually at work) until the *whole* of the ether was evaporated. The taps connected with the silver flask were then closed, the key inserted in the storage-circuit, the connexion with the Clark cells made, and the rheochord adjusted until the potential difference at the ends of the coil was shown by the high-resistance galvanometer to be equal to that of the Clark cells used. Three or four of these cells were placed in parallel arc, and the files thus formed in series: therefore, when using an electromotive force of 4 Clark cells, we had really in use 12 or 16.

Throughout an experiment the attention of my assistant * was directed to keeping the potential balance as even as possible. I meanwhile had to observe and mark the time of transit across the graduations of the bridge-wire. A reversing-key was maintained at a constant period of oscillation (about twice per second), and as the temperature rose the oscillations of a dead-beat galvanometer mirror (which were viewed through a telescope fitted with a micrometer-scale) steadily diminished, and the moment when they ceased could, to my surprise, be determined with great accuracy. By pressing a key, the time was recorded on the chronograph tape.

The mercury-thermometer inserted in the walls of the steel chamber was observed at regular intervals, any alteration noted, and a correction afterwards applied to the bridge-wire reading—the value of each division of the bridge-wire in terms of a millimetre of the thermometer-scale being known. The time of each 1000 revolutions of the stirrer was automatically recorded on the tape, thus the only notes that had to be taken during an experiment were of the changes of the mercury-thermometer. The chronograph was one of somewhat novel construction, for which I am indebted to Mr. E. A. Pochin. It was worked by a water motor, had a triple set of recording hammers, and was controlled by an electric clock which was compared at regular intervals with a "rated"

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* I take this opportunity of returning my thanks to Mr. C. Green, Scholar of Sydney College, Cambridge, for his able assistance during these experiments.

Dent's chronometer, but as the greatest gain in rate observed was less than 1 in 12,000, no correction was necessary.

I find it impossible to give a detailed record of the observations, as it would fill a volume. I therefore propose to give an example in full of one of the experiments by drawing at random one of the leaves from the mass of records.

TABLE I.

Aniline Exp. No. 26 : 4 cells. July 28th.

Cooled to reading 36 cm. b.w. Temp. of b.w. = 67°·5 F.
Temp. Clark Cells = 15°·27 C. throughout.

Experiment commenced at 1–17–30.

Bridge-wire reading in centims.	Time by chronograph.	Number of revolutions.	Time.	Time per 1000 revolutions.	Temp. by thermometer A.
	secs.		secs.	secs.	millim.
54·5	331·4				166·53
55·0	347·7	0	348·1		
55·5	366·9				
56·0	384·4				
56·5	403·4			204·5	166·55
Mean	366·8				
61·5	582·5	1000	552·6		166·58
62·0	600·5				
62·5	619·4				
63·0	638·1			204·6	
63·5	656·0				166·60
Mean	619·3				
68·0	819·9	2000	757·2		166·61
68·5	838·5				
69·0	856·2			204·2	
69·5	874·9				
70·0	892·6	3000	961·4		166·60
Mean	856·4				
75·0	1079·6			205·3	166·60
75·6	1098·7				
76·0	1118·3				
76·5	1137·4				
77·0	1156·2	4000	1166·7		166·59
Mean	1118·0				

Mean reading of thermometer A = 166·58 millim. = 16°·459 C.

Reduction of the Results.

Let θ_0 be the temperature of the surrounding envelope and θ_1 that of the calorimeter at any time t. Let the change in temperature per second due to the work done by the stirrer be σ, and let ρ equal the gain in temperature per second due to the combined effects of convection, conduction, and radiation when the difference in temperature between the calorimeter and the surrounding envelope is unity.

Let a wire whose resistance is R at θ_0 and R_1 at θ_1 be immersed in a liquid contained in the calorimeter, and let the mass of the contained liquid be M and its specific heat S_1 when the temperature is θ_1.

Let the capacity for heat of the calorimeter be w_1 when the temperature is θ_1.

Thus the thermal capacity of the calorimeter and contents at any temperature θ_1 is S_1M+w_1.

If the ends of the wire be kept at a constant potential-difference of E, then we get (paper J, p. 367):—

$$\frac{E^2}{J\,.\,R_1(S_1M+w_1)}+\{\sigma-\rho(\theta_1-\theta_0)\}=\frac{d\theta_1}{dt}.$$

Since σ is small and we can make $\theta_1-\theta_0$ of any magnitude we please, it is always possible to obtain a value of θ_1 such that $\sigma-\rho(\theta_1-\theta_0)=0$, and in that case

$$\frac{E^2}{J\,.\,R_1(S_1M+w_1)}=\left(\frac{d\theta_1}{dt}\right)_e,$$

the suffix denoting the nature of the supply.

This temperature (viz. that value of θ_1 which causes $\sigma-\rho(\theta_1-\theta_0)$ to vanish) I shall denote throughout this paper by the term "null point," by which I mean that value of θ at which the observed rate of rise is due to the electrical supply only, and I shall use θ_N to indicate that temperature.

Two or three methods of finding θ_N suggest themselves. If the stirrer be set working when there is no electrical supply, then θ_1 will gradually approximate to θ_N, and a few observations as to the rate of change in θ_1 will supply sufficient information to enable the observer to set the value near to θ_N, and the calorimeter can then be left to gradually assume the true value. I have given this method a fair trial, for the apparatus has been left working for twenty-four hours at a time, and the value of θ_N ascertained with precision.

For example, at the rate of 9·10 revolutions per second it was found that the value of $\theta_N-\theta_0$ (expressed in terms of the mean bridge-wire centimetre) was about 9·2 (*i. e.* 0°·85 C. approximately), and that when the rate was 5·00 the value was about 2·7 (=0°·25 C. approximately); and it is noticeable that the ratio 9·2 : 2·7 is nearly that of $(9{\cdot}1)^2 : (5{\cdot}0)^2$, thus indicating that the heat developed by the stirrer varied approximately as r^2, where r is the rate of revolution.

A modification of this method renders it possible to determine the thermal value of the stirring work. After obtaining θ_N as above, find what value of θ_1 will cause the temperature to remain steady when the heating effect is that due to the stirring and a potential-difference of one Clark cell. Call this temperature θ_{N_e}; we have thus two equations,

$$\sigma - \rho(\theta_N - \theta_0) = 0,$$

and

$$\sigma + \frac{e^2}{J \,.\, R_1(S_1M + w_1)} - \rho(\theta_{N_e} - \theta_0) = 0\,;$$

hence

$$\frac{\sigma}{\sigma + \dfrac{e^2}{J \,.\, R_1(S_1M + w_1)}} = \frac{\theta_N - \theta_0}{\theta_{N_e} - \theta_0}.$$

Whatever method is adopted the experiments involve much labour and time, for a redetermination of θ_N must be made for each change in θ_0, as it is probable that owing to changes in the viscosity and surface-friction of the contained liquid, θ_N would be some function of θ_0 when the rate of revolution of the stirrer is constant; and a complete determination of the value of θ_N for each value of θ_0 would have doubled or trebled the length of the investigation.

It has always appeared to me to be possible that the value of ρ is a function of the rate of change in the temperature of the calorimeter. The temperature-gradient from the calorimeter to the surrounding walls must alter slightly with the rate of change in θ_1, and the rate of loss or gain in temperature of the calorimeter must as a consequence be affected; or, in other words, I think it probable that the value of θ_N is a function of $\frac{d\theta_1}{dt}$, hence the value of θ_N obtained by experiments such as those described above, where the temperature of the calorimeter is constant, may differ appreciably from the value of θ_N when the temperature is rising.

The method I finally adopted must diminish, although it does not entirely eliminate, any error due to this change in θ_N.

Let several experiments be performed similar in all respects except that the potential-difference is changed in each case.

Let the potential-difference of a Clark cell be e, and let n be the number of cells used.

Then

$$\frac{(ne)^2}{JR_1(S_1M+w_1)}+\{\sigma-\rho(\theta_1-\theta_0)\}=\frac{d\theta_1}{dt},$$

hence

$$\left(\frac{d\theta_1}{dt}\right)\times\frac{1}{n^2}=\frac{e^2}{JR_1(S_1M+w_1)}+\frac{\sigma-\rho(\theta_1-\theta_0)}{n^2}.$$

Let us assume for the time that θ_N is independent of n, then, when $\theta_1=\theta_N$, we get

$$\frac{d\theta_N}{dt}\times\frac{1}{n^2}=\frac{e^2}{JR_1(S_1M+w_1)},$$

hence

$$\frac{d\theta_N}{dt}\times\frac{1}{n_1^2}=\frac{d\theta_N}{dt}\times\frac{1}{n_2^2}=\frac{d\theta_N}{dt}\times\frac{1}{n_3^2}=\&c.$$

where n_1, n_2, n_3 &c. are the number of cells used in each case.

If, therefore, we plot the curves (which in this case are straight lines since the variables, viz., $\rho(\theta_1-\theta_0)$ and R_1, S_1, and w_1 may for small changes of temperature be considered as linear functions of θ_1, see paper J, pp. 442–448), which we obtain by taking $\frac{d\theta_1}{dt}\times\frac{1}{n^2}$ as ordinate, and θ_1 as abscissa, they will intersect where the abscissa is θ_N, and there only, and since the value of $\frac{d\theta_1}{dt}$ can be experimentally determined for different values of θ_1, the observations themselves can be made to give the value of θ_N, and we can thus find $\frac{e^2}{J.R_1(S_1M+w_1)}$, the rise due to the electrical supply alone.

A small deviation from the true value of θ_N is of little consequence, for the resulting value of $\frac{d\theta_1}{dt}\times\frac{1}{n^2}$ will only differ from $\frac{d\theta_N}{dt}\times\frac{1}{n^2}$ by the quantity $\frac{\rho(\theta_1-\theta_N)}{n^2}$, and since ρ is small as compared with the other magnitudes, $\theta_1-\theta_N$ must be considerable before the error becomes appreciable.

As this is an important point, I will select one of the three-cell experiments (No. 37) in order to show the relative magnitude of the various quantities, and the probable limit of error arising from the assumption that θ_N is independent of n. The differences in temperature are expressed in terms of the temperature difference equivalent to 1 centim. of the bridge-wire, but would of course have the same relative values in any scale.

$$\rho = \cdot 000082.$$

$$\sigma = \cdot 000230.$$

$$\left(\frac{d\theta_N}{dt}\right) = \cdot 014670.$$

Let us assume that the value taken for θ_N differed from the true value by as much as 1 bridge-wire degree (as will be seen when the experimental results are given this is an excessive estimate), then $\theta_1 - \theta_N = 1$, hence (*supra*) the value of $\frac{d\theta_1}{dt}$ would differ from

$$\frac{d\theta_N}{dt} \text{ by } \frac{\rho(\theta_1 - \theta_n)}{n^2} = \frac{\cdot 000082 \times 1}{9} = \cdot 000009.$$

When the values of $\frac{d\theta_1}{dt} = \frac{1}{n^2}$ (where $n=2$, 3, or 4) were plotted as ordinates with θ_1 as abscissa, the resulting straight lines were found to intersect not in one but in three points, which, however, were so near to each other that (except in one case) the probable error introduced by assuming that any one intersection gave the true value of θ_N was less than that above indicated. The triangle formed by joining the three points of intersection was almost invariably of one form and of nearly equal dimensions, indicating that its existence was not due to experimental irregularities but was connected in some way with the difference in the rate of rise with different values of n. I think that my impression that ρ and hence θ_N are functions of $\frac{d\theta_1}{at}$ is thus confirmed.

In any case the error caused by the assumption that θ_N is the same with different rates of increase in temperature, must be less than the error resulting from the assumption that it is the same when the temperature is rising and when it is steady.

Again, the null point finally selected for each group of experiments was always obtained in the same manner from the three points of intersection. Any error, therefore, is of the same nature in each case, and as the specific heat was obtained by the subtraction of one ordinate from another, the effect of any error is diminished considerably. True, when the absolute value of the ordinate is used in order to obtain the water equivalent of the calorimeter, any error in the position of θ_N, and therefore in the length of the ordinate, would produce its full effect, and might be appreciable, but as regards the determination of the specific heat by the method of differences it is almost certainly negligible. It would be represented by $\frac{(\rho_1-\rho_2)(\theta_1-\theta_N)}{n^2}$, where ρ_1 and ρ_2 are the values of ρ when the masses of the liquid are M_1 and M_2; and since

$$\rho_1(M_1S_1+w_1)=\rho_2(M_2S_1+w_1),$$

the limit of error is given by the expression

$$\frac{\rho_1S_1(M_2-M_1)}{M_2S_1+w_1}\times\frac{\theta_1-\theta_N}{n^2}.$$

Now the value of $\frac{S_1(M_2-M_1)}{M_2S_1+w_1}$ in these experiments was about $\frac{1}{4}$, hence we get $\frac{\rho_1}{4}\cdot\frac{\theta_1-\theta_N}{n^2}$ as the expression for the error, and this would in no case amount to $\frac{1}{1000}$ of $\frac{d\theta_N}{dt}$.

I assume, therefore, that the values of $\frac{d\theta_N}{dt}$ given by the experiments are sufficiently approximate.

If C_b is the value, in degrees C. of the air-thermometer, of the temperature difference equivalent to 1 centim. of the bridge-wire*, then

$$\frac{d\theta_N}{dt}\times\frac{R_1\times C_b}{e^2}$$

gives the rise per second in degrees C. with unit resistance and unit potential-difference.

The reciprocal of the quantity thus found gives us T, the time of rising 1°, when $E=1$ and $R=1$.

Now

$$\frac{T}{J}=\sigma_1M+w_1.$$

Let the value of T be T_1 when M is M_1, and T_2 when M is M_2.

Then we get

$$S_1M_1+w_1=\frac{T_1}{J},$$

---

* See p. 54, *supra*.

and

$$S_1M_2+w_1=\frac{T_2}{J},$$

hence

$$S_1=\frac{T_1-T_2}{J(M_1-M_2)}.$$

We can now find the value of S_1M_1, and therefore

$$w_1=\frac{T_1}{J}-S_1M_1.$$

Thus both the specific heat of the liquid and the water-equivalent can be found if two groups of experiments with different masses of liquid have been performed at the same temperature.

Since $J=4\cdot198\times10^7$ * ergs, when the unit of heat is "the quantity of heat required to raise 1 grm. of water through 1° C. of the air-thermometer at 15° C.," it follows that the results obtained at different temperatures are all expressed in terms of that unit, and are not dependent upon our knowledge of the changes in the specific heat of water.

Corrections.

Before proceeding to plot the results the following corrections had to be made :—

I. For changes in the temperature of the steel chamber during the time of an experiment. For temperatures below 26° C. a mercury-thermometer labelled A was used, situated as described on p. 56, and 1 millim. change in A was equivalent to 4·05 millim. in the bridge-wire reading. Thermometer II. was used for temperatures above 26° C., and 1 millim. change in II. was equivalent to 5·5 millim. of the bridge-wire. The resulting correction had to be added or subtracted from the bridge-wire value of $d\theta_1$, and it rarely exceeded 0·2 millim.

II. The correction to the "mean bridge centimetre." This correction was given with great exactness by the table resulting from the calibration of the bridge-wire previously referred to. It is applied as a factor to $\frac{d\theta_1}{dt}$.

III. The normal rate of stirring during experiments 1 to 8 was 9·10 revolutions per second, for the remaining experiments 5·00. A considerable number of experiments gave $tr^2 = 800{,}000$ approximately, where r is the rate per second, and t the time of rising 1 centim. of the bridge-wire. The correction to the normal rate therefore is $\frac{r^2 - r_1^2}{800{,}000}$, where r is the normal and r_1 the observed rate.

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* Proc. Roy. Soc. lv. p. 26.

As the stirring rarely departed much from the normal this correction was always small, it in no case exceeded ·00006, and rarely exceeded ·00002; and as the values of tr^2 given by the stirring experiments did not differ by more than 1 part in 50, the correction is sufficiently close.

IV. The correction consequent on changes in the temperature of the bridge-wire. This is given with sufficient accuracy by the expression

$$\frac{d\theta_1}{dt} \times \{1 + {\cdot}00016(\theta_1 - 59)\},$$

θ_1 being measured by a Fahrenheit thermometer.

V. The correction for the temperature of the Clark cells. Assuming Lord Rayleigh's temperature-coefficient ·00077, we get $\frac{d\theta_1}{dt}\{1 + {\cdot}00154(\theta - 15)\}$; for the rate of rise varies as E^2.

VI. The subsequent operations are simplified if some arbitrary value is assigned to R′, and the consequent value of $\frac{d\theta_1}{dt}$ for that value of R′ ascertained. As the resistance of the coil increased from about 8·45 to 8·6 ohms as θ_1 increased from 15° to 50° C., it was found convenient to take 8·5 ohms as the arbitrary resistance. The correction is $\frac{d\theta_1}{dt} \times \frac{R_1}{8{\cdot}5}$.

The true value of R_1, however, is not that obtained by merely taking the resistance in the usual manner with a small current. I have in paper J, pp. 404–7, published a full account of a method of finding the increase in R′ due to an increase in the potential-difference of 1, 2, &c. Clark cells.

The increase, with this coil, was carefully determined, with the following results*:—

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* I have to thank Mr. F. H. Neville, Fellow of Sidney College, Cambridge, for his kindness in assisting me in this somewhat troublesome determination.

TABLE II.

Potential-difference (in terms of a Clark cell).	δR (in true ohms).
1	·00087
2	·00227
3	·00433
4	·00723

The resistance of the coil was carefully determined for each group of experiments, at the mean temperature of the group, and also occasionally at a fixed temperature, in order to trace any change. During the first series a slight increase was observable (apart from the natural increase due to its temperature-coefficient). This was possibly a consequence of an oversight on my part, as I had forgotten to previously anneal the wire. After it had been raised to the highest temperature attained during these experiments the further change became negligible.

The absolute value of R_1 was obtained by means of the dial-box described in paper J, pp. 408–10. The errors of the separate coils and of the coils in the bridge-arms had been ascertained by a direct comparison, which had been made by kind permission of Mr. Glazebrook, with the B.A. standards in the autumn of 1892.

VII. The value of $\frac{d\theta_1}{dt}$ at several points of the range (which was usually about 15 centim. of the bridge-wire, *i. e.* about $1^{\circ}\cdot4$ C.) having been ascertained, the results were plotted (with θ_1 as abscissa) in order to ascertain the regularity &c. of the observations, which was generally found to be satisfactory. The values of $\frac{d\theta_1}{dt}$ at the readings 60 and 70 of the bridge-wire were then obtained and divided by n^2. Three experiments having been performed at each temperature with three different values of n, the intersection of the three lines thus found gave θ_N, the ordinate for that abscissa giving the rate of rise due to the electrical supply alone. A plan of these intersections is given on Plate I.

A glance at Plate I. will show that the null point in each case is not accurately defined.

The intersection of the 3- and 4-cell lines is always to the left of the other intersections.

I have shown (p. 65) that the error introduced by this uncertainty is in any case small, more especially so as the results are deduced from differences in the ordinates. The most probable position appears to me to be about midway between the points of intersection of the 2-cell line with the other lines; but as it is improbable that the position of the point would vary capriciously as the temperature rose, I have selected points on the smoothed curve (called the "null-point curve") which passes most nearly through the various intersections.

It will be noticed that the null-point curve approaches more nearly to the outside temperature as the value of θ_1 increases*. This indicates either (1) that the work done by the stirrer had diminished (this would probably be due to diminished viscosity or surface friction); or (2) that the loss by convection, &c., had increased. The former is I think the more probable explanation.

When the depth of the liquid is increased, the stirrer has more work to do and the supply of heat is greater while the loss remains unchanged. The null point therefore is at a higher elevation when the mass is greater, and Pl. I. shows that $\theta_N - \theta_0$ is nearly proportional to the depth, *i.e.* to the mass, of the contained liquid.

In order to illustrate the method of applying the various corrections, and also to indicate their comparative magnitude, I give in full (Table III.) the working out of experiment 26, of which the details were given in Table II. The numbers in Roman numerals indicate the sections on the preceding pages, in which the particulars of the correction are given. The greatest correction is that given by the calibration of the bridge-wire, and this can be applied with great certainty.

I do not consider it necessary to crowd this paper with similar details regarding the remaining experiments. Table IV. (pp. 71, 72) is a summary in which I have given the numbers necessary for the remaining calculations.

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* This curvature is more marked than would at first sight appear from an inspection of Plate I. Owing to the difference in the temperature coefficient of the two differential thermometers, the true bridge null point is given by the expression $59{\cdot}84 + {\cdot}0003\,\theta_1$, where θ_1 is the temperature of the thermometers. The position of the bridge null point is shown by the vertical lines on the left.

TABLE III.

Showing the Corrections necessary for the Reduction of Experiment 26. July 28.

	Range on bridge-wire 55·5–62·5 cm.	Range on bridge-wire. 62·5–69·0 cm.	Range on bridge-wire. 69·0–76·0 cm.	Ref. No.
Observed time over range (t)	252·5 secs.	237·1 secs.	261·6 secs.	
Change in external temp. (therm. A) during the experiment	+·05 mm.	+·015 mm.	−·010 mm.	
Change in range consequent on change in therm. A (1 mm. A = 4·05 mm. of bridge-wire)	+·020 cm.	+·006 cm.	−·004 cm.	I.
Uncorrected rise per 1 sec., *i. e.* $\frac{d\theta_1}{dt}$	·027802	·027440	·026743	
Mean value of 1 cm. of the bridge-wire over this range in terms of mean bridge-wire cm.	1·00245	·99281	·99494	
Correction of $\frac{d\theta_1}{dt}$ to mean bridge-wire cm.	+·000068	−·000197	−·000135	II.
„ „ for temp. of Clark cells.	+·000010	+·000010	+·000009	V.
„ „ for temp. of bridge-wire.	+·000037	+·000037	+·000036	IV.
„ „ for stirring to rate 5·00.	+·000012	+·000011	+·000011	III.
$\frac{d\theta_1}{dt}$ after corrections	·027929	·027301	·026664	
Mean point of range (bridge-wire)...	59·00	65·75	72·50	
	A.	B.	C.	

Since the points thus found should lie on a straight line, the best result is arrived at by treating the results so as to obtain 2 points only. If we mean A and B, and again B and C, we attach undue value to B. The true mean is obtained by $\frac{2A+B}{3}$ and $\frac{B+2C}{3}$.

We thus get:—

Bridge-wire readings .... 61·25 cm. 70·25 cm.

Mean value of $\frac{d\theta_1}{dt}$ .... ·027720 ·026877

We can thus obtain (either arithmetically or by plotting) the values of $\frac{d\theta_1}{dt}$ at B.W. readings .... 60·00 cm. 70·00 cm.

which are .... ·027837 ·026900

Now the value of R_1 near the "null point" (about 62·5 b.w.) was found to be 8·46093 true ohms. To this add ·00720 for the rise in resistance due to a potential-difference of 4 Clark cells (Table II.); hence $R_1 = 8·4681$, hence correction to $R = 8·5000$ is −·000104 .... VI.

Hence $\frac{d\theta_1}{dt}$ at B.W. readings .... 60·00 cm. 70·00 cm.

when R is 8·5000, = ... ·027733 ·026796

and $\frac{d\theta_1}{dt} \times \frac{1}{4^2}$ = ... ·001733 ·001675

TABLE IV.

Expt.	Date.	Mass of Aniline (*in vacuo*).	Number of cells. (*n*.)	Normal rate of stirring.	Mean external temp. C.	Temp. of "null point" above exterior. $(\theta_x-\theta_1.)$	External temp. + diff. to "null point." $(\theta_x.)$	$\frac{d\theta_1}{dt}\times10^6$ after corrections I., II., III., IV., V., VI. at		$\frac{d\theta_1}{dt}\times\frac{1}{n^2}\times10^6$. (Plate I.) at		Reading on "null-point" curve.	Mean value $\frac{d\theta_x}{dt}\times10^6$.
								60 b.w.	70 b.w.	60 b.w.	70 b.w.		
1, 2, & 3.	July 12	294·99	3	9·10	16·935	+°·844	17·847	25672	24296	2853	2700	2747	2748
4 & 5.	„ 13	„	2	„	16·908	+·844	17·720	11935	11585	2984	2646	2750	
6 & 7.	July 16	358·20	3	9·10	25·072	+·862	25·934	22929	21397	2547	2377	2390	2392
8.	„ 16	„	2	„	25·069	+·862	25·931	10656	9485	2664	2371	2393	
9.	„ 24	„	2	5·00	16·375	+·184	16·559	9923	8617	2481	2154	2417	2417
10 & 11.	„ 17 24	„	3	„	16·380	+·184	16·564	21998	20763	2444	2296	2415	
12.	„ 18	„	4	„	16·379	+·184	16·563	38973	37732	2436	2358	2420	
13.	„ 18	„	3	„	25·236	+·184	25·420	21735	20476	2419	2275	2391	2395
14.	„ 18	„	2	„	25·351	+·184	25·535	9787	8677	2447	2169	2395	
15.	„ 18	„	4	„	25·274	+·184	25·458	38658	37348	2415	2334	2400	
16.	„ 20	„	2	„	32·979	+·183	33·162	9717	8448	2429	2112	2370	2370
17.	„ 20	„	3	„	32·977	+·183	33·160	21496	20255	2394	2256	2370	
18.	„ 20	„	4	„	32·968	+·183	33·151	38168	36858	2385	2303	2370	
19.	„ 21	„	3	„	40·349	+·183	40·532	21127	19849	2367	2222	2340	2345
20.	„ 21	„	2	„	40·368	+·183	40·551	9602	8357	2401	2089	2348	
21.	„ 21	„	4	„	40·379	+·183	40·562	37885	36475	2366	2280	2348	
22.	„ 22	„	3	„	50·225	+·182	50·407	20726	19496	2336	2198	2311	2314
23.	„ 22	„	2	„	50·214	+·182	50·396	9452	8256	2363	2064	2312	
24.	„ 22	„	4	„	50·211	+·182	50·391	37317	36057	2332	2253	2318	

Table IV. (*continued*).

Expt.	Date.	Mass of Aniline (*in vacuo*).	Number of cells (n.)	Normal rate of stirring.	Mean external temp. C.	Temp. of "null point" above exterior. ($\theta_N - \theta_1$.)	External temp. + diff. to "null point." (θ_N).	$\frac{d\theta_1}{dt} \times 10^6$ after corrections I., II., III., IV., V., VI. at 60 b.w.	70 b.w.	$\frac{d\theta_1}{dt} \times \frac{1}{n^2} \times 10^6$. (Plate I.) at 60 b.w.	70 b.w.	Reading on "null-point" curve.	Mean value $\frac{d\theta_N}{dt}$ $\times 10^6$.
25.	July 28	569·53	3	5·00	16·448	+·241	16·689	15665	14834	1741	1648	1710	1711
26.	„ 28	„	4	„	16·459	+·241	16·700	27733	26796	1733	1675	1713	
27.	„ 28	„	2	„	16·484	+·241	16·725	7135	6196	1784	1549	1710	
28.	„ 28	„	2	„	25·216	+·237	25·453	7050	6230	1763	1558	1695	1696
29.	„ 29	„	3	„	25·219	+·237	25·456	15557	14627	1729	1625	1696	
30.	„ 29	„	4	„	25·217	+·237	25·454	27426	26460	1714	1654	1696	
31.	„ 29	„	2	„	32·985	+·236	33·221	6966	6142	1742	1536	1679	1680
32.	„ 31	„	4	„	32·999	+·236	33·235	27245	26183	1703	1643	1684	
33.	„ 31	„	3	„	32·999	+·236	33·235	15398	14412	1711	1601	1678	
34.	Aug. 1	„	2	„	40·313	+·232	40·545	6890	6067	1722	1517	1663	1664
35.	„ 1	„	3	„	40·313	+·232	40·545	15222	14296	1691	1588	1662	
36.	„ 1	„	4	„	40·313	+·232	40·545	26983	25898	1686	1619	1666	
37.	„ 2	„	3	„	50·302	+·228	50·530	15015	14053	1668	1561	1639	1640
38.	„ 2	„	2	„	50·274	+·228	50·502	6804	5959	1701	1489	1640	
39.	„ 2	„	4	„	50·312	+·228	50·540	26535	25600	1658	1600	1641	
40.	„ 3	„	3	„	16·522	+·240	16·762	15701	14806	1745	1645	1712	1712
41.	„ 3	„	4	„	16·549	+·240	16·789	27708	26766	1732	1673	1712	
42.	„ 3	„	2	„	16·532	+·240	16·772	7120	6200	1780	1555	1713	

The value of $\frac{d\theta_\pi}{dt}$ having been ascertained as above indicated, the capacity for heat of calorimeter and contents is easily deduced.

The operations are shown in Table V.

Col. I. gives the temperature of the null point in degrees C. of the air-thermometer (from Table IV.).

„ II. the rate of rise at the null point as deduced from the group of experiments at that temperature (from Table IV.).

„ III. the value of the mean centimetre of the bridge-wire at the temperature of the null point, denoted by C_b.

„ IV. gives the rate of rise when $R=1$ true ohm and the potential-difference 1 volt ($e=1{\cdot}4342$, $e^2=2{\cdot}0570$), expressed in degrees C. of the air-thermometer. The value of R' used in this reduction is 8·4966 instead of the 8·5 ohms which was selected as a convenient arbitrary value of R' in the reductions in Table IV. The two wires connecting the roof of the calorimeter with the steel lid had a total resistance of ·0068 ohm. We may assume that half the heat generated in these wires passed into the steel lid, and half into the calorimeter. We may therefore consider their resistance as ·0034 ohm$=r$. Now the points which were kept at a constant P.D. were at the lid of the calorimeter and between these wires and the coil. The equation is $J.H.=\frac{E^2}{R_1}\left(1+\frac{r}{R_1}\right)t$; hence the effective resistance $R_1-r=8{\cdot}5-{\cdot}0034$.

„ V. gives the reciprocals of the numbers in Col. IV.

„ VI. The value of J is assumed as 4·198 *. The numbers in this column give the capacity for heat of calorimeter and contents expressed in terms of "a thermal unit at 15° C." The results when plotted as ordinates, with θ_1 as abscissa, are shown in Plate II (a).

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* Proc. Roy. Soc. vol. lv. p. 24 (1894).

TABLE V.

Experiments.	I.	II.	III.	IV.	V.	VI.
	θ_N.	$\frac{d\theta_N}{dt} \times 10^6$.	C_b.	$\frac{d\theta_N}{dt} \times \frac{R' \times C_b}{e^2} \times 10^7$.	T.	$\frac{T}{J}$
1 to 5 ...	17·784	2748	·09040	10265	974·2	232·05
6 to 8 ...	25·933	2392	·09062	8952	1117·0	266·08
9 „ 12 ...	16·562	2417	·09037	9020	1108·6	264·10
13 „ 15 ...	25·471	2395	·09061	8964	1115·6	265·77
16 „ 18 ...	33·158	2370	·09081	8890	1124·9	267·97
19 „ 21 ...	40·548	2345	·09102	8816	1134·3	270·22
22 „ 24 ...	50·398	2314	·09129	8722	1146·5	273·12
25 to 27 ...	16·705	1711	·09037	6387	1565·7	372·99
28 „ 30 ...	25·454	1696	·09061	6348	1575·3	375·30
31 „ 33 ...	33·230	1680	·09082	6300	1587·1	278·10
34 „ 36 ...	40·545	1664	·09102	6251	1599·8	381·11
37 „ 39 ...	50·524	1640	·09129	6185	1616·8	385·14
40 „ 42 ...	16·780	1712	·09037	6390	1564·9	372·80

Remarks on Tables IV. and V.

Experiments 1 *to* 3 (3 *cells*) *and* 4 *to* 5 (2 *cells*) were performed with a view to testing the working of the various portions of the apparatus, and in order to ascertain the minimum quantity of liquid that could be used with safety. The results were not satisfactory: the values of $\frac{d\theta_1}{dt}$ at the same temperature, when deduced from the different experiments in which the conditions were similar, differed considerably, occasionally by as much as 1 per cent. The cause was evident: the depth of liquid was too small to give satisfactory results with this form of stirrer. Considerable difficulty was experienced in maintaining the potential balance, and it is possible that at times portions of the coils were uncovered. I therefore decided on increasing the depth of the liquid.

Experiments 6 *to* 8.—The mass of aniline was now increased by about 60 grms., and the observations became more satisfactory. These experiments were performed with a stirring rate of 9·10 per second. I had not yet decided upon the best method of ascertaining the null point, and unfortunately did not perform any 4-cell experiments. When deducing the results, I assumed that the intersection of the 2- and 3-cell lines stood in the same relative position to the intersection of the 2- and 4-cell lines as was found in those cases where a 4-cell experiment had been performed.

The null point is of course (see Plate I.) in a very different position from that found when the stirring-rate was 5·00; and the close agreement between the results given by these three experiments at the high rate, and experiments 13 to 15 at the same temperature but with a slow rate, is a satisfactory proof of the validity of this method of finding θ_N.

Experiments 8 *to* 39 call for no special comment. They were all conducted with a stirring-rate of (approximately) 5·00; Nos. 9 to 24 with the same mass of aniline as 6 to 8. From No. 25 upwards the mass of aniline was increased to 569·53 grms.

On plotting the values of the capacity for heat of this mass of aniline and the calorimeter, the spot obtained from experiments 25 to 27 appeared in a somewhat abnormal position; consequently, although I had considered the experimental work as completed, I decided to repeat these experiments, and Nos. 40, 41, and 42 give the result. They agree so closely with the corresponding group as to confirm the position originally assigned to the curve at that temperature (about 16°·7 C.).

The curves on Plate II. (*a*) give the capacity for heat of the different masses of aniline together with the calorimeter, at different temperatures. Both of the curves resulting from the larger masses show a marked change between 15° and 25° C. It is worthy of notice that the specific heat as deduced from these curves shows little or no signs of any similar change, but that it appears very markedly in the water-equivalent curve, and in such a manner as to indicate that it was approaching a minimum. Had I not been able to determine the specific heats by methods independent of the behaviour of the calorimeter, I should have concluded that the temperature coefficient of the specific heat of aniline altered considerably at the lower temperatures.

This indicates the necessity for extreme caution in similar investigations.

Table VI. gives a summary of the results, obtained from the values given by the curves in Plate II. (*a*).

TABLE VI.

Col. I. gives the capacity for heat of calorimeter +358·20 grms. (*in vacuo*) of aniline.
„ II. gives the capacity for heat of calorimeter +569·53 grms. (*in vacuo*) of aniline.
„ III. is the difference between the numbers in Cols. I. & II., and is therefore the capacity for heat of 211·33 grms. (*in vacuo*) of aniline.
„ IV. the specific heat of aniline at the respective temperatures.
„ V. the water-equivalent of the calorimeter.

Temp. θ_1.	I. $S_1M_1+w_1$. $M_1=358{\cdot}20$.	II. $S_1M_2+w_1$. $M_2=569{\cdot}53$.	III. $S_1(M_1-M_2)$. M_1-M_2 $=211{\cdot}33$.	IV. S_1.	V. w_1.
15°	263·82	372·38	108·56	·5137	79·82
18	264·36	373·13	108·77	·5147	80·02
20	264·74	373·69	108·95	·5155	80·11
25	265·80	375·14	109·34	·5175	80·44
30	267·10	376·88	109·86	·5198	80·90
35	268·50	378·82	110·32	·5221	81·49
40	270·02	380·86	110·84	·5244	82·19
45	271·58	382·90	111·32	·5268	82·88
50	273·00	384·88	111·88	·5294	83·39
52	273·55	385·63	112·08	·5304	83·60

Experiments 1 to 5 give $\frac{T}{J}=232{\cdot}05$ (Table V. *supra*) when $M_3=294{\cdot}99$, and $\theta_1=17^\circ{\cdot}78$ C. From the above table we get $w_1=80{\cdot}01$ when $\theta_1=17^\circ{\cdot}78$.

Hence

$$\begin{aligned} S_1M_3+w_1&=232{\cdot}05\\ w_1&=\underline{\ \ 80{\cdot}01}\\ \therefore\ S_1M_3&=152{\cdot}04 \end{aligned}$$

hence $S_1=\underline{{\cdot}5154}$ (*cf.* with ·5146 *supra*).

Again, the early experiments with water (p. 57) gave :—

$$\begin{array}{lll} \text{when} & \theta_1=17{\cdot}2 & w_1=80{\cdot}1\\ \text{and} & \underline{\theta_1=17{\cdot}2} & \underline{w_1=79{\cdot}8}\\ \text{hence when} & \theta_1=17{\cdot}2 & w_1=\underline{79{\cdot}95} \end{array}$$

(*cf.* with 79·99 *supra*).

Although I have referred to experiments 1 to 5 as unsatisfactory in themselves, the value obtained from them is (as above pointed out) in fair agreement with that deduced from the remaining experiments.

The same remark applies to the absolutely independent determinations of the water-equivalent when conducted with water itself, and they afford strong corroborative testimony as to the accuracy of the conclusions.

The following simple formula gives the specific-heat curve with sufficient accuracy:—

$$S_t = 0{\cdot}5156 + (\theta_t - 20) \times {\cdot}0004 + (\theta_t - 20)^2 \times {\cdot}000002. \quad \text{(A)}$$

The following table gives the experimental results and those obtained from the above formula.

TABLE VII.

θ_t.	S_t (Experimental Results).	S_t (from formula A).
15°	·5137	·5137
20	·5155	·5156
25	·5175	·5176
30	·5198	·5198
35	·5221	·5221
40	·5244	·5244
45	·5268	·5269
50	·5294	·5294
52	·5304	·5305

I have made a careful search for records of previous determinations, but I have been unable to find any in addition to those given in Landolt and Börnstein's tables—which are as follows:—

Temp.	S_t.	Observer.
8° to 82°	·5120	Schiff.
12° to 138°	·5231	„
12° to 150°	·464	Petit.

NOTE (*Sept.* 6, 1894).—Having unfortunately strained one of the leads when the tank was at a high temperature, the insulation between the coil and the steel chamber commenced to fall off on Sept. 1st. I have therefore most reluctantly been compelled to take the whole apparatus to pieces, in order to replace the ebonite insulators. On Sept. 3rd I withdrew the whole of the aniline, and on examining it I found that in colour it had darkened considerably. The experiments described in this paper were completed on Aug. 3rd and on Aug. 16th the apparatus was again set going, and was kept continually at work until Sept. 3rd. During this time electrical currents were continually passing through the coil and the stirrer must have made some millions of revolutions. The nature of the experiments that I was then engaged upon compelled close attention to the capacity for heat of the aniline, and I am convinced that even a small change in the specific heat could not have escaped my notice. It would appear, therefore, that the change indicated by this darkening was not of a nature to sensibly affect the specific heat.

[An additional Note will be found among the Miscellaneous Articles in the present Number.]

III. *A Method for Comparing the Values of the Specific Inductive Capacity of a Substance under Slowly and Rapidly Changing Fields: Results for Paraffin and Glass.* By EDWIN F. NORTHRUP*.

[Plate III.]

MAXWELL'S electromagnetic theory of light entails the relation that the square of the index of refraction of a substance, for infinitely long waves, shall equal its specific inductive capacity. But as the refractive index has only been obtained for very short waves (excepting some experiments upon the refractive index of a few dielectrics for electric waves), it is not unexpected that this relation should not hold in the case of many substances whose specific inductive capacity has been determined in steady or very slowly alternating fields. It is to be expected, however, if the field of force under which the value of K is obtained could be made to alternate at a rate which would produce waves comparable in length to the waves with which the refractive index is determined, that the agreement of K and μ^2 required by the theory would be obtained. The experiments of Professor Hertz upon electrical oscillation have suggested certain methods for determining the specific inductive capacity under fields changing at a rate which approaches that required. No research, however, aiming at a direct comparison of the values of K under slowly changing and oscillating fields, which is as fully conclusive as could be desired appears to have been made. The objects held in view in the following investigation were :—1st. To perfect a method which will enable the specific inductive capacity of solids (for which substances the value of K departs most from the required relation) to be determined under fields of force varying slowly or rapidly as desired ; and 2nd. To employ the method on one or two substances, to learn if the agreement with the theory is closer in the latter than it is in the former case. With the method under consideration this comparison may be made with the same apparatus and under conditions similar in all essential features.

Description of Apparatus.

Fig. 1, Pl. III., gives in elevation the apparatus employed. Fig. 2 in plan. The dimensions of the parts are given in the diagram in centimetres. The following are its essential features:—Three heavy brass plates, A, B, and C (fig. 1), each 12 × 14 inches, are fastened parallel to one another, and are capable of being separated each from the other through a range of several inches. Each plate is held in position by four insulating strips of ebonite which extend out from its edge; four iron rods, with a screw-thread cut upon their entire length, pass through the ends of the ebonite strips, which may be secured in any position upon the rods by bolts one above and one below each strip (figs. 1, 2, and 3). At the centre of each of the two outside plates, and perpendicular to them, is fastened a heavy brass tube. A rod, half of which is brass and half ebonite, slides in this tube, the ebonite portion extending between the plates; and the whole is capable of being moved in the tube by means of a rack and pinion. A scale, divided into twentieths of a centim., is marked upon the brass portion of the rod, and a vernier is attached to the side of a section cut in the tube. Each of the ebonite rods carries at its end between the large plates a thin plane plate of glass; its surface facing the centre plate being covered with a thin metal foil. These two small plates are as nearly as possible parallel to the parallel large plates, and their position between them is given by the vernier scale. The two outside plates, B and C, are connected by a brass rod, as shown in fig. 1. At the centre of this rod is a brass ball kept well polished, which is capable of adjustment towards or away from the centre plate, by having the ends of the brass rod made to slide in tubes fitted to the two outside plates. The ball may also be rotated about the rod as an axis, or moved up and down. Another ball, nearly opposite the first, is fastened to the centre plate by a short metal pin, which permits it also to be rotated. This arrangement of the two balls allows them to have a wide range of adjustment in relation to each other, and permits different portions of their untarnished surfaces to be brought opposite.

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* Communicated by the Author.

This apparatus is arranged as follows:—The two outside plates are connected to the earth. One terminal of a large induction-coil is also connected to the earth, while the other is attached to the ball, *n*, which is fastened to the centre plate. When the balls are separated about 6 or 8 millim., sparks pass between them when the coil is put in operation.

We have here an oscillating electric system. The lines of force divide themselves between the two halves of the apparatus, reaching from the centre plate to the two outside plates. In the region of the small plates, the field may be considered as practically uniform. Hence, if these two small plates are at equal distances from the centre plate, which we consider for the present as midway between the outside plates, they are always at the same potential with respect to each other.

If a slab of dielectric be now placed upon the centre plate and beneath the movable plate, it will have two effects: 1st, to make the capacity upon its side of the centre plate greater than it is upon the other side; and, 2nd, to raise the potential at any point above it to a higher value than is the potential at a corresponding point upon the opposite side of the middle plate. Therefore, in order to keep the two small plates at an equal potential in reference to each other, they must be placed at unequal distances from the centre plate. The value of the specific inductive capacity of a substance is deduced in a manner presently to be shown, from the relative positions of these plates. Either one or two slabs of dielectric may be used, and several different dispositions may be given to the apparatus in a manner serving to prove the correctness of the determinations.

As the object of the experiment is to make a *comparison* of the values of the specific inductive capacity when obtained under slowly and rapidly oscillating fields, it becomes necessary, in obtaining the value under the latter condition, to completely separate out any slow changes in potential, which the centre plate may be subject to, from the rapid changes which take place when oscillation occurs, and which alone are to be made use of. It follows as a consequence of the large self-induction of the secondary of the induction-coil, that the potential of the plate to which the coil is attached rises slowly at first, until, finally, it becomes sufficiently high to break down the dielectric of the spark-gap; the rapid oscillations occurring only during the passage of the sparks. The following method was successfully employed to tell when the movable plates had the same potential in reference to each other, and to "weed" out the effects of the rapid oscillation to be used from any effects of slow changes in potential which might take place.

Two fine wires were led from the movable plates to the primary of a highly insulated transformer which was distant about 2½ feet from the apparatus (figs. 1 and 2). The secondary of the transformer had its terminals end in a spark-gap. This was made by approximating the points of two needles, fastened to the end of a small slab of paraffin held in a wooden clamp. One needle was made to slide in a fine glass tube, to allow the length of the spark-gap to be readily adjusted. It may be mentioned here that any device which has an appreciable capacity as compared with that of the movable plates cannot be employed to show when these plates have the same potential, if the spark-gap is used directly connected to the plates; and such is the case when the apparatus is used with slowly varying fields. When the plates are connected with the primary of the transformer, it is not a disadvantage to add capacity to the secondary. However, after trying a large number of devices such as a telephone, electrometer, electroscope, &c., a spark-gap was found to be the simplest, most accurate, and in all respects the most convenient arrangement both with slowly changing and oscillating fields. One reason why the spark-gap best serves the purpose is because it requires at least 300 volts to make a spark pass, and consequently small and irregular alterations in potential are not shown. An electrometer-needle, on the other hand, keeps up a continual oscillation which is very confusing. A lens was adjusted in front of the spark-gap, and the room darkened when readings were taken. The transformer which was finally adopted, after many trials of different forms, consisted of fine wire wound upon two glass tubes which slid over each other; the wire upon the inner one forming the primary, that upon the outer one the secondary. The inside tube was 1½ inches in diameter and 7 inches long. This tube was given a thin coating of paraffin to insure high insulation; and in this was traced, with the aid of a lathe, a uniform spiral groove, there being in all 55 turns, 16 to the inch. No. 42 copper wire was wound in this groove, and the ends, soldered to terminal loops of somewhat larger wire, were secured at the ends of the tubes with drops of sealing-wax. The secondary, made in the same manner, consisted of 116 turns of wire of the same size, wound in a groove 35 turns to the inch. When all is in proper adjustment for oscillating fields, and the two small plates are at unequal potentials, bright sparks pass at the detector spark-gap, whenever *rapid oscillations* in the potential of the centre plate occur. If, however, the two balls (p and n, fig. 1, Pl. III.) are so far separated that no sparks can pass between them, the potential of the centre plate is then only varying at a slow rate and no sparks pass at the detector spark-gap, for the change of induction in the secondary is not sufficiently rapid to raise the potential to the 300 volts or more required to break down the dielectric. This point was carefully tested by working the coil—which had a sparking distance of 4 inches—to its full capacity and so placing the movable plates as to be always at the greatest difference of potential in reference to each other. Unless sparks passed between the balls, no sparks whatever passed at the detector spark-gap. But whenever sparks did pass between the balls, so that rapid oscillations were taking place, bright sparks at the spark-gap always occurred. This was considered proof that whenever the transformer was employed, only the effects of the rapid oscillations were being observed.

If, now, the transformer is dispensed with, and the wires from the movable plates are connected directly to the spark-gap, and the two balls (*p* and *n*, fig. 1) are separated so that no sparks can pass between them, then evidently we have a slowly changing field, and the movable plates are, as before shown, at the same potential in reference to each other when the sparks go out at the detector spark-gap. The manner of taking the observations and the results obtained will be given after describing the mathematical theory of the method.

THEORY OF THE METHOD.

The apparatus may be disposed in two distinct ways :—1st. Where one block of dielectric is used which is placed in the apparatus, as shown in fig. 1. 2nd. Where two equal slabs of dielectric are used and disposed, as shown in fig. 4.

CASE I.— *Where one Slab of Dielectric is used.*

Let V be the potential at any instant of the plate A, while the potentials of B and C are always kept at zero. Let the adjustable plates, M and N, be so placed as to have partitions upon opposite sides of A where the potential at any instant is V_1. Then for the side AB of the double condenser,

$$-\int_{V}^{V_1} dV = \frac{4\pi\sigma'}{K}\int_0^{d_1} dx + 4\pi\sigma'\int_{d_1}^{d_1+d_4} dx ,$$

where K is the specific inductive capacity of the dielectric to be measured (K, fig. 1), and d_1, d_4 are the distances shown in fig. 1, and σ' is the surface-density upon the upper side of plate A. This gives

$$V - V_1 = \frac{4\pi\sigma'}{K} d_1 + 4\pi\sigma' d_4. \quad . \quad . \quad . \quad . \quad (1)$$

Likewise for the condenser AC,

$$V - V_1 = 4\pi\sigma d_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where σ is the surface-density upon the lower side of plate A.

Equating the second members of (1) and (2) we obtain

$$K = \frac{\sigma' d_1}{\sigma d_2 - \sigma' d_4}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Considering a unit area in the middle of plate A, $\sigma' = e'$

for the upper side of the plate, and $\sigma=e$ for the under side, where e' and e are the quantities of electricity upon unit area of the respective sides. Whence we have for the capacities c' and c of unit areas of the two sides, $c'=e'V=\sigma'V$ and $c=eV=\sigma V$, and $\sigma'=\frac{c'}{V}$, and $\sigma=\frac{c}{V}$. Substitute these values for σ' and σ in (3), and

$$K=\frac{c'd_1}{cd_2-c'd_4}\text{. . . . . } \quad (4)$$

Now, if the dielectric is as large as the plates, and these are not too far apart, the field may be taken as uniform over an area, A, equal to that of one of the small plates, M or N.

Hence,

$$c'=\frac{A}{4\pi\left(\frac{d_1}{K}+d_4+d\right)}, \text{ . . . . . . } \quad (5)$$

and

$$c=\frac{A}{4\pi(d_2+d_3)}\text{. . . . . } \quad (6)$$

Substitute these values of c' and c in (4) and

$$K=\frac{\dfrac{d_1}{\frac{d_1}{K}+d_4+d}}{\dfrac{d_2}{d_2+d_3}-\dfrac{d_4}{\frac{d_1}{K}+d_4+d}}\text{. . . . . . } \quad (7)$$

Reduced,

$$K=\frac{d_1d_3}{dd_2-d_3d_4}\text{. . . . . } \quad (8)$$

d_4 may be taken $=0$, and then

$$K=\frac{d_1d_3}{dd_2}\text{. . . . . } \quad (9)$$

We shall now determine the best thickness to give to the dielectric so that errors made in adjusting the plate N will produce the smallest error in deducing the value of K. The errors made in measuring d and d_1 may be neglected in comparison with the error made in setting the plate N. Now, taking the case where $d_4=0$, and where each pair of large plates are the same distance apart,

$$K=\frac{d_1d_3}{d(D-d_3)}\text{. . . . . . } \quad (10)$$

Here D is the total distance between either pair of large plates. The variation in the value obtained for K when d_3 varies from its true value is the error. Call the error E. Then

$$\frac{\partial K}{\partial d_3}=E=\frac{Dd_1}{d(D-d_3)^2}, \quad . \quad . \quad . \quad . \quad (11)$$

from (10)

$$d=\frac{d_3d_1}{K(D-d_3)}.$$

Substitute this value of d in (11), and we obtain

$$E=\frac{KD}{d_3(D-d_3)}. \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The error is least when $\partial E=0$. Differentiating (12) we obtain

$$\partial E=\frac{-KD(K-2d_3)\partial d_3}{d_3^2(D-d_3)^2},$$

which, put $=0$, gives

$$d_3=\frac{D}{2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

This says that a variation of d_3 from its true value produces the minimum error in the value deduced for K when the plate N is halfway between the two large plates A and C. To have the plate in this position the following relations must hold :—

$$d_3=d_2=\frac{D}{2}=\frac{d+d_1}{2},$$

and from (9)

$$K=\frac{d_1}{d}.$$

Whence we obtain

$$\frac{D}{2}=\frac{\frac{d_1}{K}+d_1}{2},$$

or

$$d_1=\frac{K}{1+K}D. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

This result, of course, can only be of value when K is approximately known.

CASE II.—*Where two equal Slabs of Dielectric are used.*

In this case plate A (fig. 4) is placed exactly midway between the plates B and C. Two equal slabs of dielectric are used, one being placed upon C, the other upon A. The thickness of the blocks of dielectric and the distances between BA and CA are determined by considerations respecting the approximate value of K for the dielectric. If these distances are correctly taken, positions may be found for plates N and M where they are always at the same potential, and where they are approximately in the centre of the spaces between the plates and the dielectric.

The plate N is supported on three small ebonite posts upon the slab D. Or, in the case of any other substance than glass, a hole may be bored through the dielectric, through which the ebonite rod which carries N may pass. The capacities of the two sides of the apparatus will now always remain equal, for if the field alternates at different rates, both dielectrics will change their specific inductive capacities equally. The formula giving the value of K is then obtained as follows:—

For the side AB,

$$-\int_{V}^{V_1} dV = \frac{4\pi\sigma}{K}\int_{0}^{d_1} dx + 4\pi\sigma\int_{d_1}^{d_1+d_4} dx\,;$$

whence

$$V - V_1 = \frac{4\pi\sigma}{K} d_1 + 4\pi\sigma d_4. \quad . \quad . \quad . \quad . \quad (15)$$

For the side AC,

$$V - V_1 = 4\pi\sigma d_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Equate (15) and (16), and we obtain

$$K = \frac{d_1}{d_2 - d_4}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Use of Apparatus according to First Method.

According to the theory given under Case I., the value of K may be obtained when the capacities of the two sides of the apparatus are unlike and unknown. It was found, however, unless the apparatus is so disposed that the capacities of the two sides are nearly equal, that the value of K obtained is not quite exact in the case of slowly varying fields, and that with oscillating fields no result whatever can be obtained. The formula is based upon the assumption that static conditions hold. Now the formula assumes that, when the centre plate has a given potential, the surface-density of each side of the plate is proportional to the capacity of the corresponding side of the apparatus. This, however, is not strictly true. As the alternations grow more rapid, the average surface-densities upon the two sides of the middle plate tend to become equal, though the capacities of the two sides of the apparatus are unlike. Moreover, if the capacities of the two sides differ largely, there is such an interference of waves, when rapid oscillations are taking place, that no position can be found for the movable plates where their potentials in reference to each other will always be equal, and consequently the sparks in the detector spark-gap cannot be made to disappear. This difficulty is not observable if the capacities are made nearly the same. It becomes necessary then, in using the apparatus with one slab of dielectric, to have the capacities of the two sides approximately equal. This adjustment can be made in a manner to be shown presently.

In taking observations by this method we proceed thus: The plates M and N are first brought into contact with the centre plate and the zero positions upon the scales are determined. The block of dielectric to be tested is then placed upon the plate A, and plate M is brought to rest upon it. The reading upon the vernier scale gives the thickness of the block. Great care, of course, is taken to cut this block so that its two faces are parallel. We may now leave plate M resting upon the dielectric or give it any desired position above it. The wires leading from N and M are first connected directly to the spark-gap and the balls, *p* and *n*, are so far separated that no spark can pass between them. In the experiment as tried, two large coils were connected in series so as to make the period of the slowly changing field as long as possible. The coil being set in action, the sparks at the detector spark-gap are observed, and the plate N is slowly moved up and down until a point is found where the sparks entirely disappear. There is a distance of about 2 millim. through which the plate may be moved without the sparks appearing. A reading is taken at the upper and at the lower limit of this space, and the mean taken as the true reading. The limits of accuracy of the method are confined to the accuracy with which this setting of the plate N can be made. Any other error should be attributed to crudeness in the construction of the apparatus, and not be considered as intrinsic to the method. These readings so taken, give by applying formula (8) an approximate value of K for slowly changing fields. The capacities of the two sides may now be made nearly equal by approaching the two lower plates until they are the proper distance apart. This distance is determined as follows:—Using the nearly correct value of K just obtained, we have for the capacity of the side AB, taking $d_4=0$,

$$C_1=\frac{A}{4\pi\left(\frac{d_1}{K}+d\right)}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (18)$$

For the side AC,

$$C=\frac{A}{4\pi D}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (19)$$

Equating the right-hand members of (18) and (19), we obtain

$$D=\frac{d_1+Kd}{K}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (20)$$

This value of D, then, makes the capacities of the two sides the same, within the limits in which K is known. A still closer value of K may now be obtained as before. Two adjustments of the apparatus are sufficient for an accurate determination. If the adjustment is exactly right σ and σ' cancel out in expression (3), and hence

$$K=\frac{d_1}{d_2-d_4}.$$

Readings should now be taken with the different values given to d_4. The closeness of the agreement of the values of K then obtained furnish a test of their accuracy.

To obtain, next, the value of K under oscillating fields we proceed as follows:—The two balls, *n* and *p*, are approached so that sparks can pass between them, the distance being chosen such that the best conditions may exist for oscillations taking place. The movable plates are then connected to the primary of the transformer, and the spark-gap to the secondary. Great care should be taken that the primary leads are symmetrically arranged and of the same length, and that no conductor be near them. Carelessness on this point led for some time to conflicting results. Waves of energy should reach the transformer along both leads at the same instant, which they will not do if the leads are of unequal length. The plates are set by means of the spark-gap, as in the case of slowly changing fields. If the value of K comes out much smaller than in the case of slow fields, another adjustment of the apparatus may be necessary. This being made, another determination can be made for slowly varying fields, using formula (8), which for small differences in the capacities of the two sides gives results correct within the limits of other necessary errors. Thus, after the apparatus has been correctly arranged, a comparison by this method of the values of K under slowly changing and oscillating fields is possible, without changing the plates. However, if the capacities are equal for the two sides when slowly changing fields are used, it was found by a careful test that the simple formula, $K=\frac{d_1}{d_2-d_4}$, may still be used when the field is oscillating, although the capacities of the two sides are now slightly different. The reason for this is that with oscillating fields the average surface-densities upon the two sides of the centre plate are the same, and hence cancel out of formula (3). The proof of this rests upon the fact that K was found to be the same for all positions of d_4, and this would not be the case if the formula were incorrect. Thus, as shown,

$$K=\frac{d_1\sigma'}{\sigma d_2-\sigma' d_4}.$$

Let $\sigma=\sigma'\pm\Delta\sigma'$, then

$$K=\frac{d_1\sigma'}{d_2(\sigma'\pm\Delta\sigma')-\sigma' d_4}=\frac{d_1}{d_2-d_4\pm\frac{\Delta\sigma'}{\sigma'}d_2}. \quad . \quad . \quad (21)$$

Now whenever d_4 is changed d_2 must change. Hence if $\Delta\sigma'$ has any value, K must change with d_4 if calculated by the formula $K=\frac{d_1}{d_2-d_4}$, but as a series of tests showed, using the simple formula to calculate the value of K, that its value did not change, $\Delta\sigma'=0$, $\sigma=\sigma'$; and hence under the conditions stated, the simple formula, $K=\frac{d_1}{d_2-d_4}$, may be used.

Use of the Apparatus according to the Second Method.

The disposition of the apparatus discussed under Case II. admits of results being obtained more quickly and satisfactorily than in the one just described, and should be preferred to the other if two equal slabs of dielectric are obtainable. Readings are taken in the same manner as with the other disposition of the apparatus. The results may be tested in a variety of ways which are readily suggested by the above discussion.

Observations upon Paraffin.

The first substance experimented upon was hard paraffin-wax. The block used was a little larger than the plates and 4·34 centim. thick. Its melting-point was determined to be 54½° Centigrade. Only one suitable block was readily obtainable, and so the first method was employed. Previously to obtaining the final result many different dispositions of the apparatus were tried, and the method tested in most of its features. Experiments were also made upon a block of paraffin smaller than the large plate; but it was found that the results were incorrect in this case, which fact makes it necessary to use blocks of the same size as or larger than the plates of the apparatus.

In obtaining the final values, the apparatus was adjusted so that $d_2+d_4=3{\cdot}51$ centim., and D was changed until the capacities of the two sides were nearly equal. In all cases superior and inferior readings were taken as previously described, and the mean taken as the true reading. The following characteristic set of ten readings, taken with slow fields, are given to illustrate the accuracy with which the plate may be adjusted. One scale-division = ½ centim.

d_4 = 2 scale-divisions.

1	13·82
2	14·32
3	13·80
4	14·20
5	13·78
6	14·22
7	13·80
8	14·22
9	13·79
10	14·20

14·015 = mean.
8·450 = zero-reading of scale.

5·565 = d_2.

The final values obtained for paraffin are embodied in the following table. The value for slow fields differs a trifle from that published in a preliminary article; further experience with the apparatus having led to the present value.

SLOW FIELDS.

d_4 in scale-divisions.	Number of Readings.	K.
0	20	2·316
1	20	2·334
2	20	2·322
3	20	2·303
Total . .	80	Mean . . 2·319

Called K=2·32.

Oscillating Fields.

d_4 in scale-divisions.	Number of Readings.	K′.
0	50	2·256
1	50	2 244
2	50	2·254
3	50	2·255
Total . .	200	Mean . . 2·252

Called K′=2·25.

Thus K for paraffin is 3 per cent. less in oscillating fields than in slowly varying fields.

Observations upon Glass.

Plate-glass seems to be the most important substance upon which to experiment, as its specific inductive capacity has been found very different by different observers, and because the values of K found for it are much greater than the square of its index of refraction. The greatest pains were taken to obtain certain results for this substance; and as the values obtained differ considerably from those found by other observers, it is hoped my readers will pardon the mention of some tedious details.

The second method was employed as described under Case II. Twelve plates of American plate-glass were used, six plates being placed in each half of the apparatus. By making the proper selection of plates for each side, the two piles were made of the same thickness. The density of this glass was determined with a Jolly balance and found to be 2·678. All measurements of dimensions were made with an excellent pair of vernier calipers and repeated a large number of times. Referring to fig. 4 for the meaning of the letters, the following dimensions were employed. These are all given in scale-divisions which equal one half the metric system :—
$P=10{\cdot}21$, $d_1=11{\cdot}964$, $d_2=5{\cdot}010$, $d_4=\chi$.

In order that there might be no springing of the plates after all had been adjusted, eight ebonite posts were placed at the corners as shown in fig. 4. The plate N was supported upon three thin tubes of ebonite. All surfaces where there could be any harmful leakage of electricity, such as along the supports to the plates M and N, were covered with a thin coating of paraffin. The small plates were connected to the spark-gap or transformer with two No. 36 bare copper wires, each $2\frac{1}{2}$ feet long. These wires were supported near the spark-gap at the ends of glass rods covered with paraffin. The transformer and spark-gap were also carefully insulated by glass and paraffin. These precautions are necessary by reason of the fact that a small leakage of electricity from the surface of the small plates changes the reading in a marked manner. Leakage of electricity, however, could be seen by darkening the room, and could also be detected by a peculiar manner in which the sparks went out. This was carefully looked for and avoided. In making the test with oscillating fields, half of the readings were taken with the transformer in one position and then the other half were taken with the ends of the transformer reversed, and the mean of the two series taken as the true reading. This becomes necessary unless the primary and secondary of the transformer are symmetrically arranged in reference to each other. Indeed it was found that the readings could be perceptibly changed by sliding the secondary coil over the primary into different positions. It is easily seen, however, that if the primary and secondary always have the same relation, and the connexions to the primary are reversed after half the readings are taken, the error is eliminated in the mean of all the readings. The current through the coil was at times large and again small, and also occasionally reversed; but these changes, as expected, did not affect the results. The length of the indicator spark-gap could also be changed without affecting the mean reading. Readings for slow fields were taken in sets of ten and averaged. The mean of twenty such sets, taken with slow fields, was 3·097. The greatest departure from the mean was +·09. Finally, from (17), when $d_1 = 11{\cdot}964$, $d_2 = 5{\cdot}010$, $d_4 = 3{\cdot}097$, we obtain $K = 6{\cdot}254$.

Called $K = \underline{6{\cdot}25}$.

The value was next obtained for oscillating fields, no change being made in the apparatus, except to connect in the transformer and approach the balls to the proper distance for sparks to pass and cause oscillations. Readings were taken in sets of twenty each. Following is the average of each of the sets taken:—

10·982
10·910
11·052
10·970

The connexions to the transformer were now reversed:—

11·030
11·052
11·000
10·998

10·999 = mean of 160 readings.
8·030 = zero-reading of scale.

2·969 = d_4.

$d_3 = 5·010$, $d_1 = 11·964$, and hence $K' = 5·861$.

Called $K' = 5·86$.

These results, then, give the specific inductive capacity of plate-glass 6·2 per cent. less in oscillating than in slowly changing fields.

Though the relative values of K for glass under these two conditions seemed to be undoubtedly correct, it was not expected to find such a low value for slow fields; and so, to verify the results obtained, the apparatus was taken apart and put together again with the dimensions changed and the experiment repeated for slow fields. The distances chosen were $P = 6·401$, $d_2 = 3·524$, $d_1 = 11·964$; and as the result of thirty readings $d_4 = 1·574$. Whence $K = 6·14$, or 1·8 per cent. less than before.

These results show that there is a decrease in the value of K for paraffin and glass when the alternations of force are rapid, but that the change is much smaller than several observers have stated. M. Blondlot found K for glass in oscillating fields to be 2·84. J. J. Thomson obtained for glass the value 2·7 (see 'Recent Researches in Electricity and Magnetism,' by J. J. Thomson, p. 471 and following). Ewing found the value of mirror-glass by a method of oscillations (Physical Review, July and August 1894, p. 51) to be 5·84. His calculated value for glass was 6·24.

The above method, it is believed, is capable of giving accurate results if the apparatus be well made, and it is hoped that the detailed description given above will enable anyone to readily repeat the experiment. Should this be done, I would suggest that the apparatus might with advantage be made considerably smaller.

I desire to say, in conclusion, that I am greatly indebted to Professor Henry A. Rowland for suggestions, and especially for the opportunity of performing the experiment*.

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* The entire original idea of this method and all its details are due to Mr. Northrup, and only one or two very minor points are my own.—HENRY A. ROWLAND.

IV. "*Densities in the Earth's Crust.*"

By J. Brill, *M.A.*[*]

IN the seventeenth chapter of his 'Physics of the Earth's Crust,' the Rev. O. Fisher has investigated an arrangement of the densities and thicknesses of the different layers composing the Earth's crust, which would give, to a high degree of approximation, a uniform value for gravity over the Earth's surface. As attempts have recently been made, in the pages of this Journal and elsewhere, to criticise the method of investigation, it occurred to me that it might be desirable to give an independent investigation of the equations obtained by Mr. Fisher. This might possibly serve to render the meaning of the work clearer than is done in the book.

In the chapter referred to above the central nucleus is supposed to consist of concentric spherical shells of uniform density, so that it will only be necessary to consider the portion outside this, which we will hereafter refer to as the "crust." We will suppose this portion to consist of m layers, whose densities, commencing from the outermost, are respectively $\rho_1, \rho_2, \ldots, \rho_m$. We will also use the symbols $k_1, k_2, \ldots, k_m$, to denote the distances of the lower surfaces of the respective layers from the Earth's surface, these distances being measured along a radius of the Earth. This will be more convenient than taking symbols to denote the thicknesses of the layers. Since we suppose the layers forming the crust to be of varying density and thickness, we see that the ρ's will vary from one radius to another, as also will the k's, with the single exception of k_m. We must suppose k_m constant, as we have laid down that the inner surface of the Earth's crust shall be a sphere concentric with the outer one.

Let O be the Earth's centre, and P a fixed point on its surface. We will take OP as the axis of polar coordinates, and consider the vertical component of the attraction at P of a polar element taken somewhere within the crust. If ρ be the density of the element we are considering, this will be represented by the expression

$$\rho\frac{r^2 \sin\theta(a-r\cos\theta)}{(r^2-2ar\cos\theta+a^2)^{\frac{3}{2}}}\,dr\,d\theta\,d\phi,$$

a being the Earth's radius.

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[*] Communicated by the Author.

We will change the variables in this expression by writing $\cos\theta=\mu$ and $r=ah$. The expression then becomes

$$a\rho\frac{h^2(1-h\mu)}{(1-2\mu h+h^2)^{\frac{3}{2}}}dh\,d\mu\,d\phi,$$

where we have rejected the negative sign that arises in the transformation from θ to μ, as we afterwards intend to integrate with regard to μ in the direction in which that variable increases.

Now, if h be less than unity, as it is in the case we are considering, we may write

$$\frac{1}{(1-2\mu h+h^2)^{\frac{1}{2}}}=1+hP_1+h^2P_2+\ldots+h^nP_n+\&c.,$$

and therefore

$$\frac{\mu-h}{(1-2\mu h+h^2)^{\frac{1}{2}}}=\mu+h(\mu P_1-1)+\ldots+h^n(\mu P_n-P_{n-1})+\&c.$$

Now, we have the formula

$$(2n+1)\mu P_n=(n+1)P_{n+1}+nP_{n-1},$$

and therefore

$$\mu P_n-P_{n-1}=\frac{n+1}{2n+1}(P_{n+1}-P_{n-1}).$$

Thus we obtain

$$\frac{\mu-h}{(1-2\mu h+h^2)^{\frac{1}{2}}}=\mu+\tfrac{2}{3}h(P_2-1)+\ldots+\frac{n+1}{2n+1}h^n(P_{n+1}-P_{n-1})+\&c.$$

If we differentiate this with respect to μ, we deduce

$$\frac{1-\mu h}{(1-2\mu h+h^2)^{\frac{3}{2}}}=1+\tfrac{2}{3}h\frac{dP_2}{d\mu}+\ldots+\frac{n+1}{2n+1}h^n\left(\frac{dP_{n+1}}{d\mu}-\frac{dP_{n-1}}{d\mu}\right)+\&c.$$

$$=1+2hP_1+\ldots+(n+1)h^nP_n+\&c.,$$

since

$$\frac{dP_{n+1}}{d\mu}-\frac{dP_{n-1}}{d\mu}=(2n+1)P_n.$$

Thus the expression for the portion contributed to the value of gravity at P by our element is

$$a\rho\,dh\,d\mu\,d\phi\{h^2+2h^3P_1+\ldots+(n-1)h^nP_{n-2}+\&c.\}.$$

Imagine a solid element cut out of the crust by radii drawn from the Earth's centre to all points of the contour of a polar surface-element drawn upon the Earth's surface. The portion contributed to the value of gravity at P by our solid element can be obtained from the above expression by direct integration. We will not write down the whole series, but only the term obtained by the integration of that containing h^n. The other terms can be deduced from this. The value of this term will be

$$a\,d\mu\,d\phi\frac{n-1}{n+1}\mathrm{P}_{n-2}\mathrm{K},$$

where

$$\mathrm{K}=\left\{1-\left(1-\frac{k_1}{a}\right)^{n+1}\right\}\rho_1+\left\{\left(1-\frac{k_1}{a}\right)^{n+1}-\left(1-\frac{k_2}{a}\right)^{n+1}\right\}\rho_2$$
$$+\ldots+\left\{\left(1-\frac{k_{m-1}}{a}\right)^{n+1}-\left(1-\frac{k_m}{a}\right)^{n+1}\right\}\rho_m.$$

We will now introduce the following assumptions :—

$$(\rho_1-\rho_2)k_1+\ldots+(\rho_{m-1}-\rho_m)k_{m-1}+\rho_mk_m=a\mathrm{A}_1,$$
$$(\rho_1-\rho_2)k_1^2+\ldots+(\rho_{m-1}-\rho_m)k_{m-1}^2+\rho_mk_m^2=a^2\mathrm{A}_2,$$

. . . .

. . . .

. . . .

$$(\rho_1-\rho_2)k_1^p+\ldots+(\rho_{m-1}-\rho_m)k_{m-1}^p+\rho_mk_m^p=a^p\mathrm{A}_p,$$

where $\mathrm{A}_1, \mathrm{A}_2, \ldots, \mathrm{A}_p$ are constant throughout the entire extent of the crust. The first $(p-2)$ terms of our series expressing the portion contributed to the value of gravity at P by our solid element, may then be written

$$a\,d\mu\,d\phi\{\mathrm{C}_1+2\mathrm{C}_2\mathrm{P}_1+\ldots+(p-2)\mathrm{C}_{p-2}\mathrm{P}_{p-3}\},$$

where

$$\mathrm{C}_1=\mathrm{A}_1-\mathrm{A}_2+\tfrac{1}{3}\mathrm{A}_3,$$
$$\mathrm{C}_2=\mathrm{A}_1-\tfrac{3}{2}\mathrm{A}_2+\mathrm{A}_3-\tfrac{1}{4}\mathrm{A}_4,$$

. . . .

. . . .

$$\mathrm{C}_{p-2}=\mathrm{A}_1-\frac{p-1}{1\,.\,2}\mathrm{A}_2+\frac{(p-1)(p-2)}{1\,.\,2\,.\,3}\mathrm{A}_3-\ldots+(-1)^{p-1}\frac{1}{p}\mathrm{A}_p.$$

The $(p-1)$th term of the series may be written in the form

$$a\,d\mu\,d\phi(p-1)\mathrm{P}_{p-2}(\mathrm{C}_{p-1}+\mathrm{U}),$$

where

$$\mathrm{C}_{p-1}=\mathrm{A}_1-\frac{p}{1\,.\,2}\mathrm{A}_2+\frac{p(p-1)}{1\,.\,2\,.\,3}\mathrm{A}_3-\ldots+(-1)^{p-1}\mathrm{A}_p,$$

and

$$U=\frac{(-1)^p}{p+1}\left\{(\rho_1-\rho_2)\left(\frac{k_1}{a}\right)^{p+1}+\ldots+(\rho_{m-1}-\rho_m)\left(\frac{k_{m-1}}{a}\right)^{p+1}+\rho_m\left(\frac{k_m}{a}\right)^{p+1}\right\}.$$

Similarly we can obtain expressions for the remaining terms. Now

$$\int_0^{2\pi}\int_{-1}^{+1}P_n\,d\mu\,d\phi=2\pi\int_{-1}^{+1}P_n\,d\mu=0,$$

if n be a positive integer. Hence that portion contributed to the value of gravity by the crust, which does not depend on the position of the point P, will be $4\pi a C_1$. Besides this there will be a minute residual effect, the most important term in whose expression will be

$$a\int_0^{2\pi}\int_{-1}^{+1}uv\,d\mu\,d\phi,$$

where

$$u=(\rho_1-\rho_2)\left(\frac{k_1}{a}\right)^{p+1}+\ldots+(\rho_{m-1}-\rho_m)\left(\frac{k_{m-1}}{a}\right)^{p+1}+\rho_m\left(\frac{k_m}{a}\right)^{p+1},$$

and

$$v=(-1)^p\left\{\frac{p-1}{p+1}P_{p-2}+pP_{p-1}+\frac{(p+1)(p+2)}{1\,.\,2}P_p+\&c.\right\}.$$

We cannot evaluate this term until we know the manner in which u depends upon μ and ϕ. As μ and ϕ vary the quantity u will experience discontinuities in its variation, but it is doubtful if anything of the nature of an abrupt discontinuity would arise. If such discontinuities arise they must be rare. Of course at the seaboard there is an abrupt variation in the density of the topmost layer, but the depth of the sea is at first quite small as regards our problem, and afterwards increases with a fair approximation to continuity.

We have supposed m layers to exist, but this is to be taken as the maximum number. There may be less than m in certain portions of the crust, and this may be provided for by considering certain pairs of consecutive k's to be equal throughout the said portions.

The equations introduced above as assumptions are practically the same as those discussed by Mr. Fisher. It is evident that we cannot introduce more than a certain number of these assumptions without making the crust to consist of uniform concentric shells. But, working on the assumption that this is not the case, we find that we have to stay our approximation at a still earlier point than this consideration would appear to indicate. This will be evident from a consideration of the method used on page 241 of the 'Physics of the Earth's Crust,' and its subsequent applications in chapters xvii. and xxvi. We have, in each of the cases discussed, gone to the furthest approximation allowable under the circumstances. The limitations are made perfectly clear in the book, and I do not think that there is anything to be added to this part of the work.

Finally, we see that we are left with a residual effect, which is undoubtedly very small, and it is not impossible that such an effect might exist in the case of the Earth.

V. *The Significance of Wiener's Localization of the Photographic Action of Stationary Light-Waves.* By J. Larmor, *F.R.S., Fellow of St. John's College, Cambridge*[*].

THE experiments by which Wiener demonstrated[†] that, when stationary plane-polarized optical undulations are produced in a photographic film, by reflexion of a stream of incident plane-polarized light at a metallic or other backing, the photographic action occurs at the antinodes of Fresnel's vibration-vector and not at the nodes, have been employed by its author and others to decide between the various theories of light. If for purposes of precise description we utilize the terminology of the electric theory of light, which formally includes all the other theories by proper choice of the vibration-vector, we may say that the photographic action takes place at the antinodes of the electric vector which corresponds to Fresnel's vibration, and not at the intermediate antinodes of the magnetic vector which corresponds to MacCullagh's and to Neumann's vibration.

The crucial experiment of Wiener relates to the case when the angle of incidence is half a right angle, so that the direct and reflected waves which interfere are at right angles to each other. If the vibration take place along the direction of intersection of the two wave-planes, it will present a series of nodes and antinodes; but if in the perpendicular direction there will not be such alternations of intensity. The experiment showed that when the light is polarized in the plane of incidence, the photographic plate develops a series of bands; but when it is polarized in the perpendicular plane these bands are absent.

The argument employed is that the photographic effect will be greatest at those places in the stationary wave-train where the vibration is most intense; and the conclusion is drawn from it that the actual vibration is represented by Fresnel's vector and not by MacCullagh's; in other words, that the vibrations of polarized light are at right angles to the plane of polarization. The force of this argument, as against MacCullagh's theory, would, however, be evaded if the vector of that theory were taken to represent something different from the linear displacement of the æther, or if vibrations were excited in the molecule by rotation instead of translation, or by stress, as Poincaré has pointed out *.

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[*] Communicated by the Physical Society: read November 9, 1894.

[†] Wiedemann's *Annalen*, 1890.

But as a matter of fact it seems difficult to assign any reason of the above simple kind, on either theory, in favour of the photographic disturbance occurring at the antinodes rather than at the nodes of the optical vibration. The remarkable suggestion thrown out by Lord Rayleigh some time previous to Wiener's experiments, and afterwards verified by Lippmann, that certain effects in colour photography produced by Fox Talbot and Becquerel were really due to this kind of localization of the photographic effect, is not in opposition to such a view; for the consideration adduced was simply that a localization, periodic with the waves, would, if it happened to exist, produce effects like the observed ones. At any rate, the observed localization demonstrates the important result that the effect is due to a specific dynamical action of the waves, and not to mere general absorption of the radiation.

Let us consider the actual circumstances of the case. There are about 10^3 molecules of the sensitive medium in the length of a single wave of light: thus in the stationary wave-train all the parts of a single molecule would at any instant be moving with a sensibly uniform velocity, which increases and diminishes periodically. The vibration of the molecule would thus be, were it not for the influence of differences of inertia or elasticity between its parts and the surrounding æther, very nearly a swaying to and fro of it as a whole: if it were exactly this, it could not be expected to produce any breaking up of the molecule at all. Moreover, as at the antinodes of the vibration there is movement but no stress in the medium, so at the nodes there is stress but no movement; and it does not seem at all clear that alternating stress might not be as potent a factor in disintegration as alternating motion. A representation has been constructed by Lord Kelvin † of a system in which internal vibrations can be

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* See a discussion on this subject in *Comptes Rendus*, cxii. 1891, in which MM. Cornu, Poincaré, and Potier took part.

† "Lectures on Molecular Dynamics," Baltimore, 1884.

excited by simple translation, by means of the device of an outer shell imbedded in the æther and containing inside it masses with spring connexions; and such a system might also be adjusted so as to respond to simple rotation, and therefore be excited at the nodes of the wave-train instead of the antinodes.

A theory based in this manner on difference of inertia must take the density of the æther to be very minute compared with that of matter; therefore if the molecule is to have free periods of the same order of magnitude as the periods of the incident light-waves, the elastic forces acting between the atoms and concerned in these periods must be very intense. But Lord Kelvin's well-known estimate of the rigidity of the æther on this hypothesis makes it very small compared with the ordinary rigidity of material bodies*. In fact on Pouillet's data, which imply a considerable underestimate, the energy of the solar radiation near the sun's surface is about 4×10^{-5} ergs per cubic centimetre; it easily follows that if the amplitude of the æthereal disturbance is, say, ϵ times the wave-length, the density of the æther must be about $1/10^{22}\epsilon$, and its rigidity, which is equal to the density multiplied by the square of the velocity of propagation, therefore $1/10\epsilon^2$. On an elastic solid theory it is desirable to have the density very small: thus if we adopt 10^{-2} as the maximum likely value of ϵ, the density of the æther comes out 10^{-18} of that of water, and its rigidity about 10^3, whereas the rigidity of steel or glass is of the order 10^{11}.

Now at first sight it would appear that the elastic tractions exerted by an æther of such small rigidity on an imbedded molecule swaying backwards and forwards in it, would be vanishingly small compared with the elastic forces between its constituent atoms which are concerned with free vibrations of the kind of period under consideration; and that therefore they would be quite incompetent to produce violent disturbance in the molecule. But on a closer examination this difficulty may to a considerable extent be evaded.

Let us imagine an imbedded rigid nodule of linear dimension L, and let the force necessary to displace it in the æther in any manner through a distance x be Lx. Let us compare with it a similar nodule of linear dimensions κL displaced through a distance κx. There is complete dynamical similarity between the two cases; the strains at corresponding points in the æther are equal, and therefore so are the tractions per unit area. Thus the forcive necessary in the latter case to produce the displacement κx is $\kappa^2 Lx$, and therefore to produce the same displacement x as in the previous case a forcive κLx is required. If now instead of comparing the total forcives in the two cases we compare the forcives per unit volume, an increase of linear dimensions in the ratio of κ to one diminishes this forcive in the ratio of κ^2 to one. Thus, if only the atoms are taken small enough, an æther of very slight rigidity can exert a forcive on them which, estimated per unit volume, is of any order of magnitude we please. The features of the case are in fact analogous to those of the suspension of small bodies, such as motes, in a viscous fluid medium like the atmosphere: if only the particles are small enough they will float for an indefinitely great time against the force of gravity, even be they as dense as platinum,—the only limit being in that case the one imposed by the molecular discreteness of the air itself.

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* *Cf.* Maxwell, *Encyc. Brit.*, article "Æther."

It would appear that the application of this principle does much to vivify the notion of an elastic solid æther. A medium of this kind, which is excessively rare and, as a consequence, of very feeble elasticity, would exert practically negligible tractions on the surfaces of a mass of matter in bulk, while it may exert relatively very powerful ones on the individual atoms of which the mass is composed if only they are sufficiently small, it being of course supposed that the structure of the medium itself is absolutely continuous. And it would even appear that a medium of very small density and rigidity may be competent to excite powerful vibrations in the molecules notwithstanding the strength of the forcives which hold them together.

We may thus imagine a working illustration of a ponderable transparent medium of elastic solid type as made up of very small spherical nodules of great density and rigidity dispersed through the æther and imbedded in it. We may even imagine these nodules to be collected into more or less independent groups, each of which will have free periods of relative vibrations of its own nearly independent of other groups, in the manner now well known in connexion with Prof. Ewing's model of a magnetic medium. A wave running across such a medium may excite these groups, and thus illustrate the theory of selective absorption by means of a system in which only the elasticity of the ambient medium is operative, but no other internal forcive.

The explanation of a very weak medium exciting such powerful tractions implies of course strains of enormous intensity, so that its limits of perfect elasticity must be taken enormously wide compared with anything we know in ordinary matter. The magnitude of the strains also requires that the displacement of an atom relative to the æther must be a considerable fraction of its diameter; and this is sufficiently secured by the large value of ϵ above that which is required to keep down the density of the æther, combined with the great relative density of the atom. It would thus seem to be possible to account for sufficiently large differential tractions between the component atoms of a molecule, especially if some of them lie well under the lee of others, to produce brisk internal vibration.

In this way we could imagine the construction of a sort of model illustrative of an elastic solid theory of refraction, including selective absorption and other such phenomena, in the form in which it is presented by von Helmholtz and others. In the simpler case, in which the atoms are not grouped into systems capable of synchronous free internal vibrations, let (ξ, η, ζ) denote the mean displacement of the free æther, and (ξ_1, η_1, ζ_1) that of the atoms. Then the equations of vibration assume the forms

$$\rho \frac{d^2}{dt^2}(\xi, \eta, \zeta) = c\nabla^2(\xi, \eta, \zeta) - \left(\frac{d}{dx}, \frac{d}{dy}, \frac{d}{dz}\right)p + a(\xi_1 - \xi, \eta_1 - \eta, \zeta_1 - \zeta),$$

$$\rho_1 \frac{d^2}{dt^2}(\xi_1, \eta_1, \zeta_1) = -a(\xi_1 - \xi, \eta_1 - \eta, \zeta_1 - \zeta)^{*},$$

in which $p = c'\left(\frac{d\xi}{dx} + \frac{d\eta}{dy} + \frac{d\zeta}{dz}\right)$; and the phenomena of crystalline media could be included by assuming a vector-coefficient instead of the scalar a.

The conclusion, then, is that in this limited range an elastic-solid theory of a very rare æther is not so much at fault as would at first sight appear.

A theory based on difference of rigidity without difference of inertia, after MacCullagh's manner, would have to be realized by ascribing to the atom an atmosphere of intrinsic æthereal strain, instead of endowing it with great inertia; and this could only be possible in a rotational æther, and would in fact form a mechanical representation of the electric theory. As such it must be expected to give an account of

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[*] There are introduced by von Helmholtz (*Wiss. Abh.* ii. p. 216) in addition, a forcive proportional to the absolute displacement of the atom, and a frictional one proportional to its absolute velocity. The former is derived from the idea that the heavy central masses of the atoms are unmoved by the æther, and only outlying satellites are affected by its motion. On our present view this restriction might be dispensed with, except in so far as it renders possible an illustrative theory of absorption of an analytically simple character. The consequences of the above equations are set out by various writers, *e. g.* Carvallo (*Comptes Rendus*, cxii. p. 522).

the phenomena of electricity as well as those of light[*], and in such an account is founded one of its chief claims.

A development of the electric theory has recently been essayed by von Helmholtz[†], on the basis of the formal equations of Heaviside and Hertz, in which the free æther is still supposed to be an elastic medium of excessively small density in which the dense atoms are imbedded. If such a view should turn out to be the basis of a consistent body of theory, the considerations given above with respect to the intensities of molecular tractions would have a bearing on it also.

Let us now consider more particularly the explanation that would be offered by the electric theory of light. The difference between a material medium and a vacuum consists in an altered effective dielectric coefficient. This difference is simply and naturally explained by the hypothesis that the material molecules are polar owing to their associated atoms having atomic charges equal in amount but opposite in sign, and that they therefore possess electric moments just as the molecules of a magnet possess magnetic moments. An electric force thus tends to pull the two constituents of a molecule asunder; and its full intensity is exerted in this manner, not merely its differential intensity over the range of the molecular volume. But a magnetic force has no such tendency even when we take the molecule to be magnetically polarized, because the two poles of a magnetic element cannot be dissociated from each other; the magnetic moment is thus directly associated with the atom, not with the molecule. In the case of the stationary light-waves the antinodes of the electric force are therefore places where alternating disturbances of a kind suitable to produce decomposition of the molecules are maintained, and may produce strong effects through sympathetic molecular vibration or otherwise; but at the intermediate antinodes of the magnetic force the individual ultimate atoms may be disturbed by the alternating magnetic force, but there is no tendency to separation of the constituents of the molecule. On the electric theory, therefore, there is abundant justification both for the magnitude of the effect produced, and for its localization as determined by Wiener's experimental investigation.

The theory, noticed first it seems by Weber, which ascribes molecular magnetism to the orbital rotation round each other of ionic charges, and which has very strong recommendations from the point of view of the dynamics of the æther, may form a partial exception to this statement. It leaves the question open as to whether the principal part of the magnetic moment is due to orbital motions in the atoms or to the motions of the constituent atoms in the molecules; though it suggests strongly the latter alternative. In that case there will usually be a differential magnetic action of the field as between these moving atoms; but the magnetic actions on positive and negative ions will be by no means equal and opposite, as is true of the electric actions. Thus, for example, in the limiting case of two equal and opposite ions revolving round each other, the elements of the equivalent ionic convection-currents will be at each instant parallel, and there will be no differential magnetic forcive at all; there will also be no magnetic moment; but the electric differential action will retain its full force.

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[*] *Cf.* "A Dynamical Theory . . . ," Phil. Trans. 1884, §§ 122-124.

[†] Wied. *Ann.* 1894.

It is well understood, and in accordance with this explanation, that the energy of chemical combination of atoms into molecules is almost entirely that of electrostatic attraction of their atomic charges. In fact the electric attraction between them diminishes according to the law of inverse square with increasing distance, their magnetic attraction according to the law of the inverse fourth power: if these forces are of the same order of magnitude in the actual configuration of the atoms in the molecule, the work done by the former during their combination must be almost indefinitely greater than the work done by the latter.

If we contemplate the purely dynamical basis which must underlie the descriptive explanations of the electric theory of light, it is difficult to see how there can be any place for a theory of the æther loaded by the material molecules, which dynamical views usually associated with Fresnel's theory demand. There could be no polarity in the inertia of a mere load, such as the present considerations require. On the other hand, the presence of electrically polarized molecules is effectively a diminution of the elasticity of the luminiferous medium; and I have tried to show elsewhere * that the principles of MacCullagh's theory of optics are in substantial agreement with all the general features of our electrical and optical knowledge.

It is definitely implied in the electromotive, as distinguished from an electrodynamic, character of the electric theory of light, that the atomic charges vibrate in unison with the light-waves, quite unimpeded by any material inertia of their atoms. This hypothesis is conceivable and natural, independently of any particular explanation, on the theory that the

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* *Loc. cit.* Phil. Trans. 1894.

atoms are themselves intrinsic mobile configurations of stress or motion, or both together, in the ultimate medium.

[It is not without interest to consider how far the conception mentioned above of an isotropic solid medium of very small density, with very massive minute nodules imbedded in it but exerting no direct forcives on each other, will carry us in forming a representation of optical phenomena. The theory is of the Young-Sellmeier type, because each nodule has one or more free periods conditioned by its form and by the surrounding elasticity.

On eliminating (ξ_1, η_1, ζ_1) from the equations expressed above, we obtain the vibrational equations of the æther, supposed thus loaded. Its elastic properties are found to be conserved intact, but the effective density as regards vibrations of period τ is increased by $a\rho_1 \Big/ \left(a - \frac{4\pi^2}{\tau_2}\rho_1\right)$. When the coefficient a is of aeolotropic type, by reason either of the form or the distribution of the nodules, we have effectively an isotropically elastic medium with aeolotropic inertia; this leads to Fresnel's wave-surface, provided the elasticity is labile in Lord Kelvin's sense. The theory also leads to a formula for ordinary dispersion, of the usually admitted type (Ketteler's) for isotropic media; but, on the other hand, it is in default by assigning a dispersional origin to double refraction. If we wish to include the minute effect known as the dispersion of the optic axes in crystals, it will be necessary to assume for the elastic stress between æther and matter a somewhat more general form, involving (after von Helmholtz) absolute as well as relative displacement, but always of course remaining linear.

The assumption of elasticity of labile type also allows an escape from the usual difficulties of a solid æther in the matter of reflexion. In that problem the elasticity would naturally be taken continuous across the interface, the volume occupied by the molecules being on this hypothesis extremely small compared with that occupied by the æther.

We may further amend the theory by getting rid of the difficulties associated with lability, at the same time avoiding the difficulty as to how a body can move through a perfect solid medium, if we take the æther to be a rotationally elastic fluid, and retain the material load as before.

But an essential and fundamental difficulty will still remain. It is the extremely small volume-density of the energy involved in radiation which permits a very small inertia, and consequently a small elasticity, to be assigned to the æther, and so prevents it from acting as an appreciable drag or exerting an appreciable force on finite bodies moving through it. But these very properties would incapacitate it for acquiring the very large volume-densities of energy that would have to be associated with it in order to explain electrodynamic phenomena.

Any representation which would make the æther consist of molecules of ordinary matter is open to the objection that the thermal kinetic energy of gases and other material systems must then, in accordance with Maxwell's law of distribution of energy, largely reside in it. But, on the other hand, if we hold to the view of matter which was first rendered precise by Lord Kelvin's theory of vortex atoms, namely, that the æther is the single existing medium and that atoms of matter are intrinsic singularities of motion or strain which belong to it, then there is no inducement to assume for the æther a molecular structure at all, or to make its inertia anything comparable with the inertia of the atoms on whose play the thermal energy of the movements of the matter consists. On such a theory the inertia, and the resulting kinetic energy, of the matter may be hard to explain, but it is certainly something different from the inertia of the underlying medium in which the atom is merely a form of strain or motion. On such a theory refraction, and also double refraction, will be caused by the atmosphere of intrinsic strain which represents the electric charge on the atom; and only dispersion will be assigned to the influence of sympathetic vibrations in the atoms or molecules, thus doing away with any difficulty of the kind mentioned above.

In the theory of gases the ordinary kinetic energy of the molecules represents sensible heat, and as such may be derived for example from the dissipation by friction or otherwise of the mechanical energy of ordinary masses: it is of the nature of kinetic energy of the masses of the atoms. But the store of energy which keeps up radiation is of electromotive kind, is concerned with displacing electricity, not with moving matter except indirectly; at least no consistent scheme has yet been forthcoming which includes both. It is quite conceivable that the disturbances which occur in the ordinary encounters of molecules are of far too gentle a character to excite the very powerful elasticity which on a certain form of the electric theory binds together the continuous medium taking part in optical propagation, any more than a system of solid balls rushing about in an enclosure bounded by a heavy continuous rigid solid can excite sensibly the elastic qualities of that body. The opinion has been widely supported, both on theoretical and experimental grounds, that a gas will not emit its definite radiations however high the temperature to which it is raised, unless there is chemical decomposition of the molecules going on. If that be so, the æther does not act as an equalizer of the kinetic energy between the different modes of vibration of the molecules, and the ordinary theory of gases need make no reference to the æther.

If I have understood aright, a similar view has been expressed as at any rate a possible explanation of the difficulty as to the application of Maxwell's distribution theorem in the theory of gases, by Prof. Boltzmann himself. The law of distribution of energy is perhaps unassailable for the case of molecules like small spheres, with three degrees of freedom, all translational. By including the rotational modes of freedom, which may be none at all for a monad gas, only two for a diad, and three for other types, and these possibly not complete, a sufficient number of freedoms is obtained to cover the known range of values of the ratio of the specific heats. The introduction of any vibrational types would make too many; so on this ground also it is not likely that such types can enter into those among which the thermal energy is divided.—*December* 4.]

VI. *The Rôle of Atomic Heat in the Periodic Series of the Elements.* By C. T. BLANSHARD, *M.A.**

BY a study of the latest, or most accurate data of atomic heats and melting-points I have been enabled to arrive at definite relationships between them, which I will endeavour to set forth. In *Grundzüge der theoretischen Chemie*, Leipzig, 1893, p. 106, Lothar Meyer says:—"The periods of fusibility do not coincide with those of other physical characters, are also less regular than these, but are in close relationship to the atomic volume." With regard to Dulong and Petit's law, W. Ostwald says ('Outlines of General Chemistry,' English translation, p. 177):—"We can only note empirically that the law holds good for substances with atomic weights higher than thirty."

A survey of the accompanying curve of atomic heats, made to correspond with Lothar Meyer's curve of atomic volumes, will, notwithstanding several blanks and several doubtful values, demonstrate the two following laws of atomic heat:—

1. The atomic heat decreases in any series from the monad to the tetrad element, and then increases till a maximum is reached with the heptad element.

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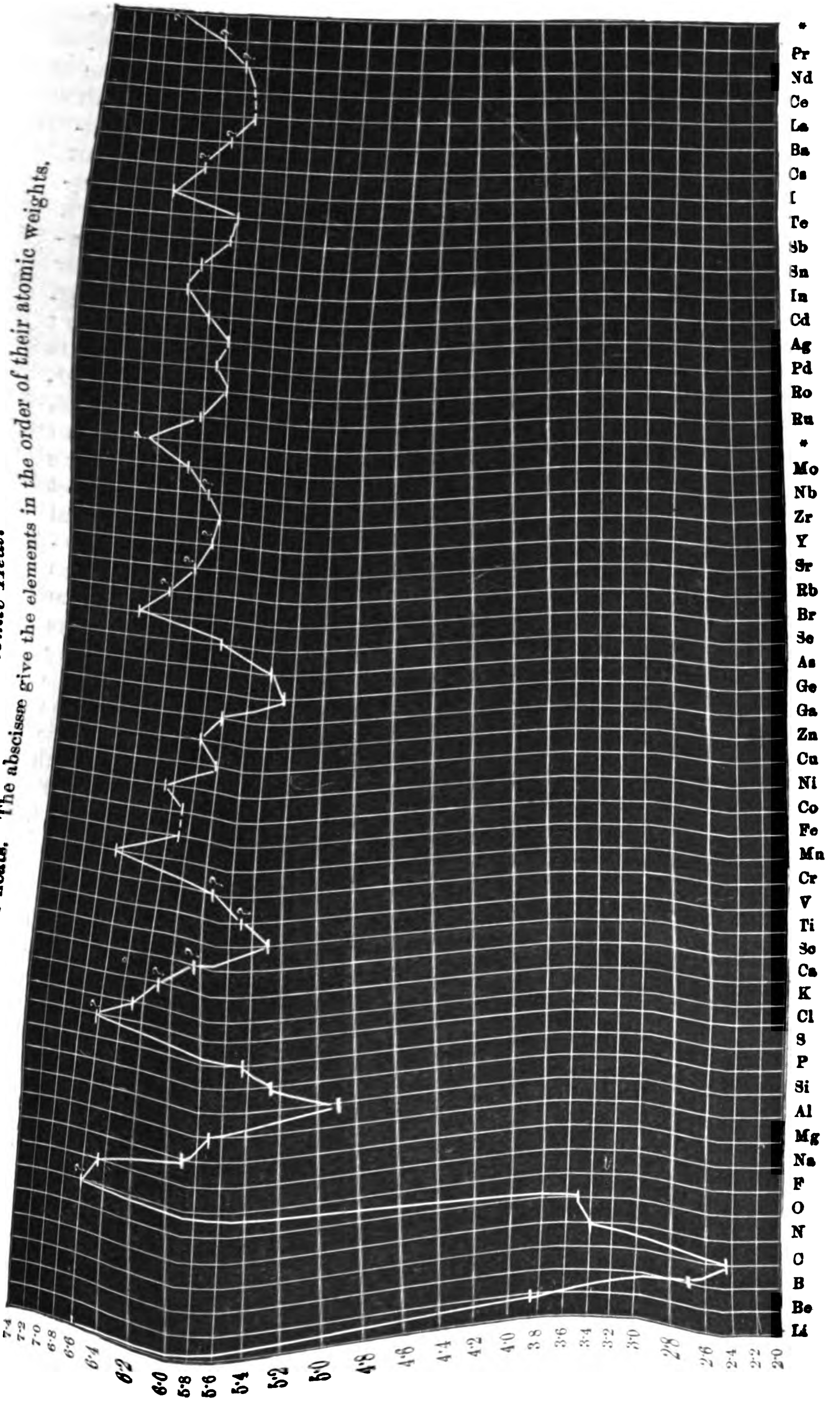
* Communicated by the Author.



Curve of Atomic Heat.

The abscissæ give the elements in the order of their atomic weights.

The ordinates are the atomic heats.

2. The variation is greatest with elements of low atomic weights, becoming less and less as the atomic weight increases.

I hope in the next place to show in a tabular form that the melting-points of the elements are intimately connected with their atomic heats, and that four general laws govern this connexion. Were sufficient data to hand with regard to latent heat of fusion &c., there is no doubt that many similar relationships would be established. There is evidently plenty of work before physical chemists in this direction. In the arrangement of the groups of elements I follow a plan used by Lothar Meyer, of using Roman numerals combined with lettering. Thus the Li group is I., the Cu is I.*a.*; Group II. is Ca &c.; II.*a* Be &c.; II.*b* Fe, Ru, Os. In placing the iron elements here, and not in a separate group, I am following W. Preyer, *Das genetische System der chemischen Elemente*, Berlin, 1893. The groups are entirely arranged by their atomic heats, but will be found to be practically identical with Lothar Meyer's classification. The melting-points taken are the most correct up to date, from (1) the late T. Carnelley's 'Physico-Chemical Constants,' 1887; (2) H. Landolt and R. Börnstein, *Phys.-Chemische Tabellen*, Berlin, 1894; (3) The Chemical Society's Journal. Several determinations are very rough, others are altogether wanting. The specific heats, which are much more complete, are from the last two sources and 'Watts' Dictionary of Chemistry.' They are all taken at as near as possible the constant t°, 15^{c}. The atomic weights are from Landolt and Börnstein and the Chemical Society's Journal. From these and the specific heats I have calculated the atomic heats with much greater accuracy than has hitherto been thought necessary. Blanks denote that no reliable data are to hand. A query denotes that the observation has been made, but not accurately.

Group.	Element.	Melting-Point.	Atomic Heat.
I.	Lithium.	180°	6·608
	Sodium.	95·6	6·526
	Potassium.	62·5	6·303
	Rubidium.	38·5	......
	Cæsium.	26·5	......
I. *a*	Copper.	1054	5·870
	Silver.	1040	5·936
	Gold.	1035	6·383
II.	*Calcium.	...	7·216
	Strontium.		
	Barium.	1100?	......

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* Bunsen's value for Ca seems too high; the atomic heat of this element will probably prove to be less than that of K.

Table (*continued*).

Group.	Element.	Melting-Point.	Atomic Heat.
II. *a*.	Beryllium.	900°?	3·85
	Magnesium.	780	5·932
	Zinc.	433·3	5·971
	Cadmium.	320·7	6·196
	Mercury.	−38·85	6·640
II. *b*.	Iron.	1550	6·104
	Ruthenium.	1950 ?	6·203 ?
	Osmium.	2500 ?	5·939
III.	*Boron.	...	2·717
	Scandium.		
	Yttrium.		
	Lanthanum.	800 ?	6·165
III. *a*.	Aluminium.	700 ?	5·741
	Gallium.	30·15	5·822
	Indium.	176	6·469
	Thallium,	288	6·735
IV.	*Carbon (amorphous).	...	2·448
	Silicon (amorphous).	1200 ?	4·9
	Germanium.	900 ?	5·32
	Tin.	232·7	6·337
	Lead.	326	6·334
IV. *a*.	Titanium.	2500 ?	5·294
	Zirconium.	1500 ?	5·979
	Cerium.	900 ?	6·161
	Thorium.	...	6·264
IV. *b*.	Cobalt.	1500	6·148
	Rhodium.	1800 ?	5·97
	Iridium.	1950	5·79
V.	Nitrogen.	−160 ?	3·40
	Phosphorus (white).	44	5·27
	Arsenic (cryst.).	300 ?	6·25
	Antimony.	432	6·155
	Bismuth.	268·3	6·27
V. *a*	Vanadium.		
	Niobium.		
	Tantalum.		
VI.	Oxygen.	−100 ?	3·47
	Sulphur (rhombic).	114·5	5·44
	Selenium (cryst.).	250	5·88
	Tellurium.	455	6·00
VI. *a*.	†Chromium.	2200 ?	5·2 ?
	Molybdenum.	2000 ?	6·336
	Tungsten.	1950 ?	6·44
	Uranium.	1700 ?	6·72
VI. *b*.	Nickel.	1450	6·32
	Palladium.	1500	6·10
	Platinum.	1775	6·04
VII.	Fluorine.		
	Chlorine.	−102	4·32
	Bromine.	− 7·3	6·72
	Iodine.	114	6·847
VII. *a*.	Manganese.	2000 ?	6·69

* The specific heats of both B and C rise rapidly with the temperature.

† W. Preyer's value for Cr is 6·2, which is entirely without foundation though it will probably prove to be nearly correct.

AUTHORITIES.

Element.	Melting-Point.	Specific Heat.	Atomic Weight.
Li ...	Bunsen.	Regnault.	Stas.
Na ...	Bunsen.	Schütz.	Stas.
K ...	Bunsen.	Schütz.	Stas.
Rb ...	Bunsen.	....	Godeffroy.
Cs ...	Setterberg (1882).	....	Bunsen.
Cu ...	Violle.	Naccari.	Richards.
Ag ...	Riemsdijk (1869).	Naccari.	Stas.
Au ...	Violle (1879).	Regnault.	Krüss.
Ca ...	....	Bunsen.	Erdmann & Marchand.
Ba ...	Frey (1876).	....	Dumas.
Be ...	Debray (1855).	Nilson & Pettersson.	Nilson & Pettersson.
Mg ...	V. Meyer & A. Meyer.	Kopp, Lorenz.	Burton & Vorce.
Zn ...	Person (1847).	Naccari.	Gladstone & Hibbert.
Cd ...	Person (1847).	Naccari.	Morse & Jones, Lorimer & Smith.
Hg ...	Vicentini & Omodei.	Winkelmann, Naccari.	Erdmann & Marchand.
Fe ...	Pouillet (wrought).	Naccari.	Erdmann & Marchand.
Ru ...	Deville & Debray.	Bunsen.	Joly.
Os ...	Joly & Vezes.	Regnault.	Seubert.
B ...	Melts in Electric Arc.	Kopp.	Abraball.
La ...	Below silver.	Hillebrand.	Bettendorff, Brauner.
Al ...	Heeren (1855).	Regnault.	Mallet.
Ga ...	Boisbaudran.	Boisbaudran.	Boisbaudran.
In ...	Winkler.	Bunsen.	Winkler.
Tl ...	Crookes.	Regnault.	Crookes.
C ...	Never melted.	Bettendorff & Wüllner.	Roscoe.
Si ...	Deville.	Weber.	Thorpe & Young.
Ge ...	Winkler.	Nilson & Pettersson,	Winkler.
Sn ...	Person.	Schütz, Lorenz.	v. d. Plaats.
Pb ...	Person.	Schütz.	Stas.
Ti ...	Never melted.	Nilson & Pettersson.	Thorpe.
Zr ...	Troost.	Mixter & Dana.	Bailey.
Ce ...	Hillebrand & Norton.	Hillebrand.	Brauner, Norton.
Th ...	....	Nilson.	Nilson & Krüss.
Co ...	Deville.	Regnault.	Zimmermann.
Rh ...	L. Meyer.	Regnault.	Seubert & Kobbé.
Ir ...	Deville & Debray.	Violle.	Seubert & Joly.
N ...	....	Regnault (as gas).	Stas.
P ...	Watts' Dict. &c.	Regnault & Person.	Schröder.
As ...	....	Bettendorff & Wüllner.	Dumas.
Sb ...	Dalton.	Schütz.	Schröder.
Bi ...	Rudberg, Riemsdijk.	Regnault.	Marignac.
O ...	....	Regnault (as gas).	Berzelius.
S ...	Brodie.	Regnault.	Stas.
Se ...	Regnault.	Kopp.	Pettersson & Eckmann.
Te ...	Carnelley.	Fabre.	Brauner.
Cr ...	Deville.	Kopp.	Rawson, Meinecke.
Mo ...	Buchholz.	Delarive & Marcet.	L. Meyer.
W ...	Wöhler.	Delarive & Marcet.	Roscoe, Waddell.
U ...	Peligot (1868).	Blümcke.	Zimmermann.
Ni ...	Carnelley & Pictet.	Regnault.	Zimmermann.
Pd ...	Violle.	Violle.	Bailey & Lamb.
Pt ...	Violle.	Schütz.	Seubert.
Cl ...	Olszewski.	Regnault (as gas).	Stas.
Br ...	Regnault, v. d. Plaats.	Regnault.	Stas.
I ...	Stas, Regnault.	Regnault.	Stas, Cooke.
Mn ...	Watts' Dict.	Regnault.	Dewar & Scott, Marignac.

The atomic heat affords another proof of Lothar Meyer's classification of sodium with the alkali metals, rather than that of Mendeléeff, who, followed by W. Preyer, places it in the copper group. Its chemical affinities to potassium are very close; thus E. Augé (*Comptes Rendus*, 1890, cx. p. 1139) obtained a sodium alum, by regulating both concentration and temperature.

To get comparable results, the specific heats must be observed at a constant temperature. With regard to melting-point, magnesium presents an irregularity in the zinc group, if the usual melting-point, 430°, is adopted; but the number has been corrected by more recent observation, restoring complete harmony to the series. The order of melting-points of Sn and Pb in Group IV., and of Sb and Bi in Group V., both apparent anomalies, will be seen to favour, rather than contradict, the laws of atomic heat and fusion; for in both cases the atomic heats are reversed to correspond with the melting-points.

I have placed cobalt in IV.*b*, and nickel in VI.*b*, notwithstanding Zimmermann's values for their atomic weights; and in doing so, as before, I have been guided entirely by the atomic heats, leading to Mendeléeff's original classification, which placed Co before Ni on purely chemical grounds, from the analogies of the former to Rh and Ir, and of the latter to Pd and Pt (*Ann.* Supp. viii. p. 133 *et seq.*). Zimmermann (1886) finds Ni=58·71, Co=58·89.

The above tables appear to establish the following laws:—

1. In groups I. and II. (which I will call the *metallic* groups), as the atomic weight increases, both the melting-point and the atomic heat decrease.

2. In groups III. and IV. and all the *a* groups (termed collectively *intermediate* groups) the atomic heat increases with the atomic weight, while the melting-point decreases; the former being characteristic of non-metals, the latter of metals.

3. In groups V., VI., and VII. (the *non-metallic* groups), as the atomic weight increases, so do both atomic heat and melting-point.

4. In the *b* groups the melting-point increases with the atomic weight, whilst the atomic heat decreases; the former being a non-metallic, the latter a metallic characteristic.

The *a* may be called *copper* groups, and the *b iron* groups.

It is to be noted that both groups IV. and V. become irregular in the same way when their last members are reached, these having more marked metallic characters. Thus both Sn and Pb in group IV., and Sb and Bi in V., have both melting-point and atomic heat in inverted order. The same order is found to hold in their latent heats of fusion. Thus Person found that tin requires 14·25 cals., whilst, according to Rudberg, lead requires only 5·8. There are no data for comparing antimony and bismuth. In the zinc group we find that the latent heat of fusion varies directly as the melting-point.

The irregularities in group III.*a* as to melting-point cannot be explained in the above manner. The elements that follow Al, viz. Ga, In, and Tl, behave, as regards atomic heat and melting-point, like the non-metallic groups.

The inverse ratio between melting-point and atomic heat in the intermediate groups is well illustrated by carbon and boron. The former, which has never been melted, has the lowest atomic heat of all solid or liquid elements; whilst the latter, which is very infusible, has the next lowest.

If the above laws are true, they should enable melting-points not yet ascertained, as of thorium, molybdenum, &c., to be predicted with tolerable accuracy. Thus, Th should melt at about 700°, Mo at about 2000°. Buchholz found this latter to be imperfectly fusible at a white heat. Again, the melting-points and specific heats of new elements should be capable of being predicted with much greater accuracy than has been possible hitherto. Thus Brauner's Bohemium (see 'Nature' for October 11, 1894) has had the specific heat of 0·03 predicted for it from Dulong and Petit's constant, but no melting-point. By referring to group VI., where it will occur after tellurium, Bo=213, it is easy to see that this element will have a melting-point of about 650° and specific heat of about $\frac{6 \cdot 1}{213} = 0 \cdot 0286$.

Volume-Heat.

The following is a carefully calculated table of volume-heats, a further factor for comparing the elements, of value for their classification, introduced by Dr. Wm. Preyer, *Das genetische System der chemischen Elemente* (Berlin, 1893).

Volume-heat is the atomic heat ÷ the atomic volume, and therefore $= CW \div \frac{W}{D} = CD$; where C is the specific heat, W the atomic weight, and D the specific gravity of the element.

The specific gravities are taken at 0°, and the specific heats at a constant temperature also, as near 15° as possible. The natural groups are those of Lothar Meyer, as modified by

W. Preyer. I have adopted Prof. Meyer's device of lettering the sub-groups, adding groups *b* and *c*, as in the preceding article. The values are from Landolt and Börnstein, *Phys.-Chemische Tabellen*, or more recent determinations.

Group I.	C.	D.	CD.	Authorities.
Lithium	0·94	0·59	0·555	Regnault, Bunsen.
Sodium	·283	·97	·274	Schütz, Gay-Lussac and Thénard.
Potassium ...	·166	·87	·144	" " " ,
Group I. *a*.				
Copper	0·0924	8·94	0·826	Naccari, various.
Silver	·0549	10·53	·578	Naccari, Rose.
Gold	·0316	19·33	·600	Violle, Rose.
Group II.				
Beryllium ...	0·424	1·85	0·784	Nilson and Pettersson, Humpidge.
Magnesium ..	·245	1·74	·426	Kopp, Lorenz; Bunsen.
Calcium	·1804	1·57	·283	Bunsen, Matthiessen.
Strontium ...	......	2·54	......	Quoted from F. W. Clarke.
Barium	......	3·88	......	" " " "
Group II. *a*.				
Zinc	0·0915	7·10	0·650	Naccari, Rammelsberg.
Cadmium ...	·055	8·55	·470	Lorenz, Naccari; Schröder.
Mercury......	·0331	13·596	·448	Winkelmann, Regnault.
Group II. *b*.				
Iron	0·109	7·86	0·857	Naccari, various.
Ruthenium ..	·061	12·63	·769	Bunsen, Joly.
Osmium	·031	22·48	·696	Regnault, Deville.
Group III.				
Boron.........	0·251	2·5?	0·627	Mixter and Dana, Hampe.
Aluminium...	·212	2·6	·551	Regnault, Naccari; Deville, Heeren, Mallet.
Gallium	·079	5·95	·470	Berthelot, Boisbaudran.
Indium	·0569	7·42	·422	Bunsen, Winkler.
Thallium ...	·0335	11·85	·397	Regnault, de la Rive.
Group III. *a*.				
Scandium ...				
Yttrium				
Lanthanum ..	0·0448	6·1	0·273	Hillebrand and Norton.
Group IV.				
Carbon ...... (diamond).	0·204	3·158	0·644	Bettendorff and Wüllner, v. Baumhauer.
Silicon (cryst.)	·177	2·39	·411	Regnault, Winkler.
Germanium ..	·073	5·469	·399	Nilson and Pettersson, Winkler.
Tin	·054	7·29	·393	Schütz, Lorenz; Matthiessen.
Lead	·030	11·352	·340	Regnault, Lorenz; Reich.
Group IV. *a*.				
Titanium ...	0·1125	......	......	Nilson and Pettersson.
Zirconium ...	·066	4·15	0·274	Mixter and Dana, Troost.
Cerium	·0448	6·65	·298	Hillebrand and Norton.
Thorium......	·0276	11·0	·303	Nilson.

Table (*continued*).

Group IV. *b*.

Cobalt	0·1045	8·6 ?	0·899	Regnault, Rammelsberg.
Rhodium ...	·058	12·1 ?	·702	Regnault, Deville and Debray.
Iridium	·030	22·42	·672	Violle, Deville and Debray.

Group V.

Nitrogen ...	......	0·90	......	Olszewski.
Phosphorus (white).	0·202	1·837.	0 371	Kopp, Pisati and de Franchis.
Arsenic (am.)	·0758	4·71	·356	Bettendorff and Wüllner.
Antimony ...	·051	6·697	·341	Lorenz, Schröder.
Bismuth	·030	9·75	·292	,, ,,

Crystalline Arsenic has the values $C = ·083$, $D = 5·73$, $CD = 0·475$ (Pettendorff and Wüllner).

Group V. *a*. Vanadium, Niobium, and Tantalum have not had their specific heats determined.

Group VI.

Oxygen	......	1·137	......	Olszewski.
Sulphur (rhomb).	0·170	2·075	0·353	Regnault, Pisati.
Selenium (cryst.).	·074	4·5	·333	Kopp, Rammelsberg.
Tellurium (cryst.).	·048	6·4	·307	Fabre, Rammelsberg.

Group VI. *a*.

Chromium ...	0·117?	6·73	0·787?	Kopp, Glatzel.
Molybdenum	·066	8·6?	·568	De la Rive and Marcet, Debray.
Uranium ...	·028	18·7	·524	Blümcke, Zimmermann.

Group VI. *b*.

Nickel	0·108	8·9	0·961	Regnault, Schröder.
Palladium ...	·057	12·148	·692	Violle, Lowry.
Platinum ...	·031	21·5	·666	Schütz, Deville and Debray.

Most observers find D for Pd as low as 11·5; Lowry's value seems reliable, and gives concordant results.

Group VI. *c*.

Erbium				
Tungsten ...	0·035	18·77	0·657	De la Rive and Marcet, Waddell.

Group VII.

Fluorine......				
Chlorine......	......	1·46	......	Knietsch.
Bromine......	0·084	3·187	0·268	Regnault; Pierre, Quincke, v. d. Plaats.
Iodine	·054	4·95	·267	Regnault, Gay-Lussac.

Chlorine is neglected, as are Oxygen and Nitrogen, because we have only their specific heats as gases.

Group VII. *a*.

Manganese...	0·1217	7·39	0·899	Regnault, Glatzel.

It will be noted from the above that in group I. the atomic heats are nearly $Li = 4a$, $Na = 2a$, $K = a$, where a is 0·144.

In group II., similarly, the ratio is $Be = 5a$, $Mg = 3a$, $Ca = 2a$.

In group VII. the volume-heats are constant.

Several elements, of known atomic weight, offer no data for both C and D, and are altogether omitted.

The above tables make clear the following laws:—

1. In each natural group of elements volume-heat varies inversely as atomic volume. (Group IV.*a* is an exception as far as available data go.)
2. The variations of volume-heat become less and less as valency for oxygen rises, until the seventh group is reached, when it becomes constant.
3. As atomic heat increases in some groups and decreases in others, with increase of atomic weight, whilst atomic volume regularly increases, it is evident that the increase in atomic volume proceeds at a higher ratio than the variation in atomic heat.
4. Atomic weight being a constant increment, it follows from the preceding law that in any natural group specific gravity varies more than specific heat.

VII. *On a Suggestion by* Professor J. J. Thomson *in Connexion with the Luminescence of Glass due to Kathode-Rays. By* John Burke, *B.A., Lecturer in Physics, Mason College, Birmingham*[*].

LAST August, at Oxford, I communicated a paper to the British Association on a strange luminous phenomenon which had been observed by Beccaria more than a hundred years ago. It was there pointed out that although the conclusions arrived at by the Italian physicist, if true, were likely to lead to results of an extremely interesting character, in connexion with Mr. Crookes' important researches on the luminescence of glass, &c., in vacuum-tubes, and although the mysterious nature of the phenomenon was likely to attract much attention, yet the subject was allowed to retain its obscurity. Beccaria ('Artificial Electricity,' § 766) observed that when *vacuum*-bulbs were broken in the dark a light, consisting of a faint glow, was produced in the place where the bulb lay. He attributed an electrical origin to the phenomenon, owing to the manner in which certain substances were supposed to behave in yielding the glow. He mentioned, moreover, that the mere breaking of glass did not give rise to the phenomenon, but that the presence of air was essential to its production, and that when air was allowed to rush suddenly into a vacuum by the bursting of a bladder at the mouth of a receiver, articles such as glass bottles, vessels of sealing-wax, &c., became luminous by, he supposed, the violent dashing of the external air on them; the luminosity was most conspicuous at the necks of the bottles or at the upper edges of the vessels.

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[*] Communicated by the Physical Society: read November 9, 1894.

As has already been remarked, Beccaria's researches appear to have been forgotten for more than a century, and not until quite recently has attention been drawn to them. This has been done by Professor J. J. Thomson, who, in his 'Recent Researches in Electricity and Magnetism,' p. 119, recalls the fact and indicates its possible close relationship to Mr. Crookes' theory of the luminescence of the glass in Geissler's tubes: that the bombardment of the glass by the particles of gas projected from the kathode is intense enough to cause the glass to become luminous. Prof. Thomson quotes from Priestley's 'History of Electricity':—

> "Signor Beccaria observed that hollow glass vessels, of a certain thinness, exhausted of air, gave a light when they were broken in the dark. By a beautiful series of experiments, he found, at length, that the luminous appearance was not occasioned by the breaking of the glass but by the dashing of the external air against the inside when they were broke. He covered one of those exhausted vessels with a receiver, and letting the air suddenly on the outside of it observed the very same light."

That the light observed in both cases was the same, unless the exhausted vessel, which had been covered by the receiver, was broken by the dashing of the external air against it, is a circumstance which, from considerations that shall presently be adduced, I think we may be justified in questioning.

Through the kindness of Prof. FitzGerald in extending to me the facilities afforded in the Physical Laboratory of Trinity College, Dublin, I have been enabled to experiment upon this subject. It would be impossible for me to attempt to render in detail the acknowledgment of what has been due to his invaluable advice and suggestions.

It must be mentioned at the outset that the present investigation has by no means been completed, yet, thus far, it appears that some of Beccaria's results have not been wholly of that degree of exactness which we should have hoped for. It must, however, be borne in mind that scientific appliances in his time were less perfect than they are to-day, and such imperfection may account for much inaccuracy.

A number of incandescent lamps of various sizes with broken filaments were procured. An observer who had been fifteen or twenty minutes in the dark, whose sight had become sufficiently sensitive to the faintest light, broke one of the larger of these bulbs with a hammer, at the same time protecting his face by a plate of thick glass. A faint *white* glow, which lasted but for a very small fraction of a second, was seen in the place where it was known the bulb had lain. The experiment was repeated in the presence of several persons, who testified to the same effect. The intensity of the light seemed to depend upon the size of the bulb—the larger bulbs, about 7 or 8 centim. in diameter, giving a greater intensity than the smaller ones; whilst with bulbs of not more than 2 centim. diameter no luminous effect was perceived.

A circular plate of glass, about 7 centim. in diameter and 2 millim. thickness, was then placed on the mouth of a receiver, the opening of which was about 5 centim. in diameter, and the contact made air-tight, whilst the air in the receiver was exhausted until a vacuum of about 20 millim. had been obtained.

The plate of glass was then broken with a hammer. A beautiful stream of white light was visible throughout the whole receiver. The light, which lasted for a small fraction of a second, resembled that produced when vacuum-bulbs were broken, though it was more distinct, and consisted not merely of a uniform glow, as in that case, but was marked, in addition, by a number of luminous spots of various sizes: in fact the effect presented the appearance of a faint nebula.

On account of the extreme faintness of the light, it was found impossible to photograph it: at least any attempts in this direction have hitherto proved unsatisfactory, even with the most sensitive plates I could procure.

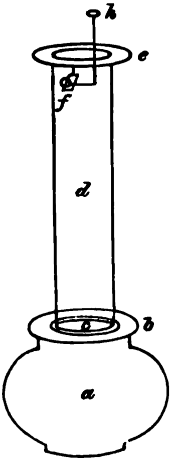
In some instances the luminous spots were observed to be unusually large; the fragments of glass were in such cases also found after each experiment to be of an exceptional size, often 7 or 8 square centim. in area.

This fact is especially worthy of notice, as it undoubtedly indicates that the fragments of glass themselves had become luminous, the continuous glow in all probability having been caused by the very minute fragments.

Different kinds of glass were used without giving any perceptible difference in the effects.

Thin brittle plates of cast-iron and steel were tried in the place of glass, but yielded negative results, owing, perhaps, to the fact that they did not break up into innumerable fragments as glass did readily when struck with a hammer, or because the air was not consequently permitted to enter the vacuum very suddenly and with sufficient violence.

Fig. 1.



Various gases were made to take the place of air. Fig. 1 represents the apparatus employed for this purpose. *a* is a glass receiver; the strong glass ring *b*, the opening of which was covered by a piece of thin glass *c*, rested on the mouth of the receiver *a*, and served to support a long glass tube *d*, at the upper end of which, being closed, there was an arrangement *e* by which a weight *f* was supported and allowed to fall by turning the handle *h* and thus break the glass *c* and open free communication between the gas in the tube *d* and that in the receiver *a*.

The joining between *d* and *a* was made complely air-tight so that no leakage occurred. The tube *d* was then filled with carbon dioxide or oxygen, and the air in the receiver *a* exhausted until a vacuum of about 20 millim. was obtained. The weight *f* was made to fall and break the glass *c*, so that the gas in *d* might enter violently into the vacuum. The same luminous phenomenon was observed as on previous occasions when air was employed, with no perceptible difference as regards colour, intensity, or the general appearance of the glow and luminous spots.

When the gases in both *a* and *d* were exhausted and the glass *c* broken as before, no luminosity whatsoever was observed, thereby showing that the mere breaking of glass did not suffice to produce the phenomenon; but that the presence of a gas was essential, though any gas was sufficient to produce the effect—that is, that some function performed by a gas in rushing into a vacuum was the cause or a circumstance invariably connected with the phenomenon.

The three following hypotheses seemed possible:—

(1) The violent dashing or bombardment of the molecules of air against the glass might have caused the latter to emit light.

(2) It might have been a sort of miniature meteorite phenomenon, caused by the collisions of the fragments of glass with the interior of the receiver and with each other; the intense bombardment of the larger fragments by the minute dust particles giving rise to the luminous spots.

(3) It might have been an electrical phenomenon caused by the rubbing of air against glass; somewhat resembling

that produced by the friction of mercury against glass in a barometric tube*.

In view of testing hypothesis (1) the following experiments were made :—

A bladder was fastened to the neck of a small receiver, the air in which was then exhausted until a vacuum of about 20 millim. was obtained.

The bladder was then caused to burst, and a stream of *yellowish* light was seen to descend within. This experiment was repeated several times with receivers of various heights; and it was found that in the case of tall receivers the light was confined to the higher portion, near the mouth of the receiver.

The intensity of the light seemed to depend upon the pressure in the vacuum, that is to say, upon the violence with which the air entered the interior of the receiver.

The general appearance of this yellowish light seemed to indicate that the luminosity in *this* case was partly, if not altogether, due to parts of the bladder taking fire, being heated by the friction of the air against them, or by being suddenly torn. Articles of various materials, such as those mentioned by Beccaria, were placed in the interior of the receiver, also a plate of glass supported horizontally so that the air on entering might impinge directly upon it.

A light in some respects, perhaps, resembling that mentioned by Beccaria was observed, but only with short receivers; for in the case of tall ones, under precisely similar circumstances, no light was perceived in the lower region where the articles lay; thus suggesting that in the former case the portions of burning bladder had been stopped, in their fall, by the articles within the receiver. Beccaria took no precautions to determine the part played by the bladder in the phenomenon, or rather, he entirely failed to notice that it ever became luminous.

In order to stop the bits of bladder, gauzes of various materials and different thicknesses were tried; such as should stop the pieces of bladder but permit the air to rush through without much impedance. The glass bottles beneath the gauze, however, were not seen to give rise to any luminosity.

A similar plan was made use of when air was allowed to enter a vacuum by the breaking of glass.

The apparatus employed for this purpose (see fig. 2) consisted of a cylindrical receiver, A; a ring, *a*, which fitted closely into the cylinder and was supported by iron rods that were adjustable so that the ring could be moved up and down, carried the wire gauze, *b*, which was tightly fastened to it. A plate of glass, *c*, was laid on the mouth of the receiver, and the contact made air-tight; *d* were articles such as glass bottles &c.; an electromagnet, *e*, supported a hammer, *f*, which fell and smashed the glass plate, *c*, when the circuit was broken at *g*. The part of the cylinder above the gauze was screened from the observer's sight.

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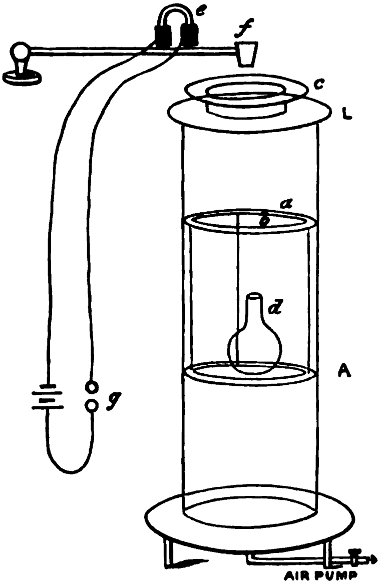
* See Armstrong, Phil. Mag. ser. 3, vol. xviii. (1844).

Fig. 2.



The air in the cylinder having been exhausted, no light was seen to penetrate the gauze, neither was there any luminosity seen in the vicinity of *d*, when the external air was allowed to enter the receiver, in the usual manner, by breaking the glass, *c*.

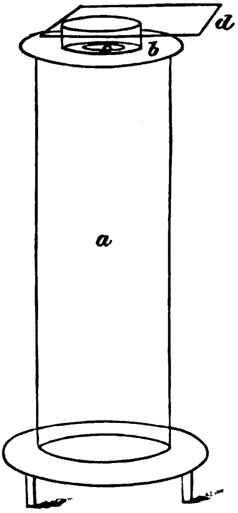
A bladder was then used instead of glass plates, but the results were similar.

Different gases were allowed to issue forth from bottles containing these gases in a highly compressed state, on the surface of glass, and especially on its sharp edges, but without producing any visible effect.

These results do not seem to harmonize with hypothesis (1). Let us now proceed to the consideration of hypothesis (2).

Fig. 3 shows the arrangement by which air could be allowed

Fig. 3.



to enter suddenly into a vacuum without the necessity for breaking glass or bursting a bladder. *a* is the glass receiver; *b* a ring, between which and the receiver is a sheet of fine tissue-paper, *c*, on which a number of fragments of glass were placed; a plate of strong glass situated on top of the ring *b* admitted of being drawn aside, and thus allowed the air to enter the vacuum, whilst the rest of the apparatus was held fast.

A luminosity similar to that seen upon previous occasions was observed, though less distinct in some respects, perhaps, than before.

Under precisely similar circumstances, in the absence of any fragments of glass on the tissue-paper, no light was produced, whether or not there were any articles that the air could impinge upon within the receiver.

A single piece of glass cut into a definite shape was then made to take the place of the great number of fragments, some cotton-wool being placed on the plate of the air-pump in order as far as possible to prevent the piece of glass from breaking.

The following facts were noticed :—(α) Only a single spark seen. Not as on a previous occasion when a number of fragments of glass were allowed to enter the vacuum, (β) the spark always appeared on the side of the receiver in the direction in which the plate *d* had been drawn aside [*] (see fig. 3). (γ) The piece of glass was found almost vertically under the place where the spark had taken place.

It seemed probable that the spark was caused by the collision of the piece of glass with the interior of the receiver. Two strong pieces of glass were then struck violently together, and a light similar in every respect to that previously observed was produced.

These experiments seem to justify hypothesis (2): the dust particles causing the glow by their impacts against the interior of the receiver and against each other; whilst the brightness of the luminous spots may be attributed to sparks produced by the larger fragments of glass, and to the bombardment of the dust particles against the surfaces of these larger fragments.

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[*] It is probable *à priori* that this should take place.

A large quantity of fragments of cast-iron, steel, ebonite, sealing-wax, bone, &c., were tried as well as glass, but the attempt to obtain a luminous effect by the above method proved fruitless.

If metallic dust should produce a luminous effect when made to bombard the surface of glass, and if different effects should be produced by lead glass and German glass, the theory that *solid* particles emitted from the kathode would give rise to luminescence of the glass would be justified. The above experiments, however, do not seem to throw much light on Mr. Crookes' theory of luminescence due to the emitted *particles of gas.*

In the earlier stage of the investigation hypothesis (3) appeared plausible enough. Any experiments, however, that were made in connexion with it did not lead to results of an interesting character.

Whatever may be the real value of these experiments, it cannot be doubted that the inquiry into the cause of such a phenomenon as that noticed by Beccaria must prove of the greatest interest: firstly, on account of the obscurity enveloping the subject, and, secondly, on account of the interest attached to the artificial production (though on a small scale) of meteoric phenomena in the laboratory.

VIII. *The Luminosity of Gases.*

By ARTHUR SMITHELLS, *B.Sc.*[*]

[Continued from vol. xxxvii. p. 259.]

[Plate IV.]

PART III.—*Experiments on the Flame-Spectra of Salts of Copper and Gold.*

IN his well-known memoir on the spectra of coloured flames Gouy (*Ann. Chim. Phys.* xviii. p. 5, 1879) draws attention to the fact that different spectral effects are obtainable from different parts of the flame of a Bunsen-burner. From his observations Gouy concludes that the inner cone of a Bunsen-flame must be hotter than the outer one, and he remarks that, though this is in some respects in accord with theory, the mechanism of the phenomenon presents serious difficulties and demands fresh researches.

The mechanism alluded to by Gouy has, I think, been explained by recent investigations on the "Structure and

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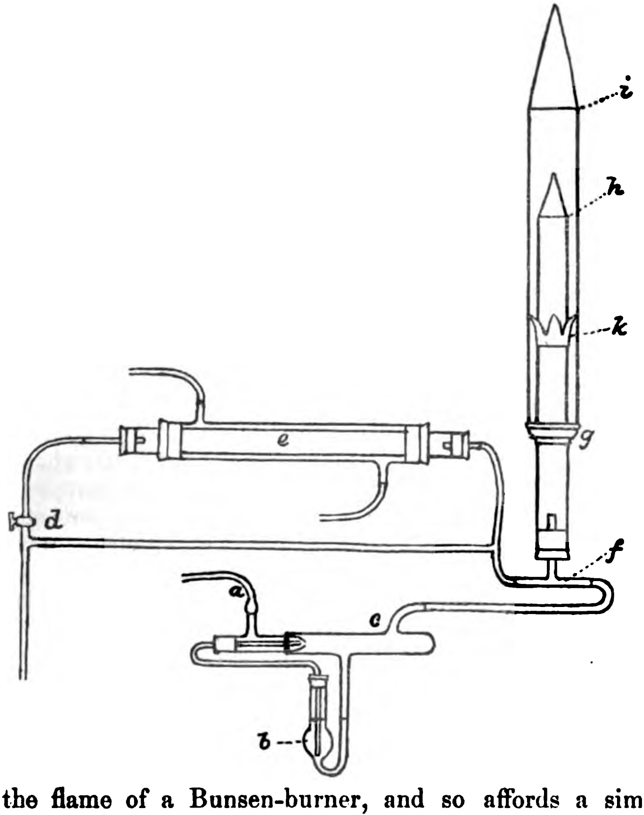
[*] Communicated by the Author.

Chemistry of Flame" (Smithells and Ingle, Journ. Chem. Soc. lxi. p. 204, 1892), from which it is clear that the flame of a Bunsen-burner must be regarded as consisting of two distinct cones of combustion. In the inner one a partial combustion of gas takes place at the expense of the oxygen of the air admitted through the air-valves: in the outer cone, such of these products of partial combustion (chiefly carbon monoxide and hydrogen) as are capable of further oxidation are burnt in the external air; but, being mixed with a large quantity of fully oxidized products and with all the nitrogen passing through the inner cone, the flame produced is of a much lower average temperature than that of the inner cone.

The apparatus used in the experiments to which allusion has just been made secures a wide separation of the cones of the flame of a Bunsen-burner, and so affords a simple means of ascertaining the different spectral effects obtainable in different parts of the flame.



The arrangement used in the experiments to be described is shown in the accompanying figure. Air under pressure is led to a Gouy sprayer (*pulverisateur*) at *a* and issues at *c*, carrying with it a fine spray or dust of the salt solution contained in *b*. The gas-supply by means of a tap at *d* can be diverted to any desired degree through a " saturator " *e*, which contains a roll of filter-paper or some asbestos moistened with any volatile acid or other liquid whose vapour it may be desired to add to the flame. The tube *e* is surrounded by a jacket through which warm water or steam may be passed, to aid in volatilizing the liquid in the saturator. The air and gas pass by a T-tube into the cone separator, which consists of two coaxial tubes connected by an india-rubber collar *g* and maintained symmetrical by the brass guide *k*. By adjusting the supply of air and gas, the flame may be so arranged that the inner cone rests at *h* and the outer one at *i*.

Flame-Spectra of Copper Compounds.

In a previous part of this paper I have commented on the difficulties of tracing the chemical processes which accompany the production of flame-spectra. The difficulties are specially great with salts of the alkalis, owing to the stability of their compounds at high temperatures. The case of chloride of copper, an easily altered substance, seemed likely to repay study, and I now give an account of the results which have been obtained.

The spectrum produced by the introduction of cupric chloride into a non-luminous flame was mapped by Bunsen and Kirchhoff in their original memoir.

In 1862 A. Mitscherlich, in a paper (Pogg. *Ann.* cxvi. p. 499) which raised the question as to the distinctive character of the spectra of compounds, described and mapped the spectra corresponding to what he called copper, copper chloride, and copper iodide. The copper spectrum was obtained by using a solution of copper oxide in acetic acid; the copper-chloride spectrum by supplying a mixed solution of copper chloride and ammonium chloride by means of a Mitscherlich-tube to a Bunsen-burner. Mitscherlich also noticed certain variations in the copper-chloride spectrum according to the quantity of hydrochloric acid present, and thought it probable that two spectra were obtainable, one of cuprous and one of cupric chloride.

In a later paper (Pogg. *Ann.* cxxi. p. 459, 1864) Mitscherlich described the spectra of copper compounds in greater detail, and mapped carefully spectra which he attributed respectively to cuprous chloride, cuprous or cupric oxide, and metallic copper. The spectrum previously attributed by him to metallic copper was now ascribed to one of the oxides of copper, and the chloride spectrum, though not particularized in the text, is indicated on the map as being due to cuprous chloride only.

In 1865 Diacon published (*Ann. Chim. Phys.* [4] vi. p. 1, 1865) a paper on "The Influence of the Electronegative Elements on the Spectra of Metals," in which he maps and describes the spectrum of cupric chloride as produced in a coal-gas flame. He mentions that the spectrum is due to the superposition of the spectra of oxide and chloride.

Lecoq de Boisbaudran, in his *Spectres Lumineux* (1874), gives a map of the spectrum obtained from copper chloride when the salt is introduced into a Bunsen-flame. In describing this map Lecoq de Boisbaudran distinguishes four cases in the use of copper chloride for the production of spectra, according to the quantity of salt employed and the length of time it is held in the flame. The particular case mapped is apparently given by the author as the one in which the normal spectrum of cupric chloride is obtained.

When in using the separator the spray of a dilute solution of cupric chloride is supplied with the air, the outer cone assumes a bright green colour; the lower cone is unaffected so far as the eye can judge (as soon as all air has been removed by diffusion from the space between the tubes), and nothing but the "candle" spectrum is seen in the spectroscope. If now a piece of asbestos soaked in hydrochloric acid be introduced into the upper cone, the green colour is replaced by a vivid blue. The same effect is obtained by introducing hydrochloric-acid gas with the gas-supply by means of the saturator. If the solution of copper chloride be replaced by one of copper sulphate or nitrate, similar effects are obtained. When these flames are examined by means of the spectroscope, the sulphate and nitrate of copper are seen to produce exactly the same result. The dilute solution of $CuCl_2$ alone gives a spectrum containing the same lines and bands as the nitrate and sulphate with the addition of other faint bands. When hydrochloric acid is supplied, the blue flame obtained gives a spectrum in which the lines and bands common to the sulphate and nitrate are very faint, whilst the additional lines just referred to as pertaining to the $CuCl_2$ flame are greatly intensified, and new lines also make their appearance. Using cold hydrochloric acid, it is impossible to entirely quench those lines which are found in the simple sulphate and nitrate spectra. But if the hydrochloric-acid saturator be jacketed by steam, or, more simply, if chloroform be used in the saturator, these lines can be entirely eliminated. We have, then, to deal with two distinct spectra—one given by copper salts in the entire absence of hydrochloric acid; the other given when a large quantity of hydrochloric acid or chloroform vapour is supplied to the flame. In the intermediate case when there is some hydrochloric acid—but not an excess—a mixed spectrum is obtained. It is obvious that one of these spectra corresponds to the oxide of copper and the other to the chloride.

These spectra have been carefully mapped * and compared with the maps of previous observers, with the following results (see Plate IV.).

1. The chloride spectrum corresponds almost exactly to that given by Mitscherlich. He failed to map three bands at the most refrangible end and to split up into three distinct bands a region between λ 460 and 480.

2. The oxide spectrum bears a general resemblance to that given by Mitscherlich, but with the exception of three bands he did not map in any detail the vague bands of which this spectrum is largely composed. One band at the least refrangible end is entirely omitted by Mitscherlich.

3. Lecoq de Boisbaudran's map comprises all the chloride lines and bands, with the exception of two on the extreme violet which he mentions but does not map, and all the bands of the oxide except those which it is impossible to discriminate in the presence of a strong chloride spectrum.

4. Diacon's map contains all the chloride lines and bands, but the oxide bands are only vaguely marked.

In addition to the appearances above described, there is one other noticeable when using copper salts in the separator with hydrochloric acid. When the flame of the outer cone is turned blue by hydrochloric acid, a dull ruddy fringe is seen to surround it. This becomes more developed as the quantity of hydrochloric acid is increased. It gives a faint luminous spectrum, chiefly in the red. As this red fringe is never obtained except in the presence of a large quantity of hydrochloric acid or chloroform and a copper salt, it seems natural to ascribe it to a compound of copper and chlorine.

It seemed desirable to inquire further into the chemical changes involved in the production of the different spectral

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* The readings of the instrument employed (a two-prism Steinheil spectroscope) have been plotted to the scale $\frac{1}{\lambda^2}$, which while giving readings referred to a natural standard presents the spectrum very much as seen with a glass-prism spectroscope.

effects, and to determine if possible to what definite compound each particular effect was due.

The effect of introducing a bead of cupric chloride into a Bunsen-flame has been carefully described by Lecoq de Boisbaudran (*Spectres Lumineux*, p. 156). As already stated, he distinguished four cases, but of these we need only take the first, in which a large quantity of salt is used. The salt first melts, and then in a few moments is seen to be surrounded by a brilliant patch of yellow, like a piece of ordinary candle-flame; the exterior parts of this patch are reddish (again resembling carbon luminosity). Outside the yellow a bright blue colour appears, and outside this the flame is coloured green. The yellow luminosity is of short duration, the blue lasts longer, but soon the only tint remaining is the green.

These three effects were so local and distinct that it seemed possible to collect the substances to which they were due, and this was done by holding in the flame glass or porcelain basins filled with water. The deposit obtained in this way from the yellow part of the flame was red in colour, it transmitted greenish light, it could be burnished, it dissolved in nitric acid with evolution of red fumes, and in fact answered in every respect to metallic copper. The yellow luminosity observed with a large quantity of cupric chloride in a Bunsen-flame must, therefore, be attributed to the liberation and incandescence of minute particles of solid copper.

The deposit obtained from the blue part of the flame was of a very pale yellow colour when freshly formed. On standing or by breathing upon it, the film absorbed moisture and became quite white: it answered in all its properties to cuprous chloride containing a little of the cupric salt.

The green part of the flame produced a deposit which was almost black and corresponded in appearance and chemical properties to cupric oxide. As the film was very thin, the possibility of it having been originally cuprous oxide and having subsequently oxidized was not excluded.

From these experiments it is obvious that the three distinct colour-effects noticeable when cupric chloride is introduced into a Bunsen-flame correspond to three different substances, viz., metallic copper, cuprous chloride, and an oxide of copper.

It is highly improbable from a chemical point of view that cupric chloride when introduced into a flame should afford a spectrum. The easy decomposability of this salt and the stability of cuprous chloride (which is volatilizable without change) would lead one to anticipate the decomposition of $CuCl_2$ into Cu_2Cl_2 and Cl_2 long before there could be any question of incandescence. That this is the case can be easily seen by holding a bead of cupric chloride well above the tip of a small Bunsen-flame, and supporting above it a porcelain basin filled with cold water. Though no flame is seen the salt melts and volatilizes sufficiently to give a considerable film on the basin, which, on examination, is seen to be almost wholly cuprous chloride.

Taking it as established that the blue part of the flame is due to cuprous chloride, the question arises, How does this salt become converted into oxide of copper to which the green part is due? This could be easily accounted for by the action of steam upon the chloride. That this is the correct explanation is established with something like certainty by experiments with flames of combustibles containing no hydrogen. In the flame of carbon monoxide or carbon bisulphide, cupric chloride produces almost exclusively the blue colour; whilst in flames of hydrogen in which, according to the hypothesis, the existence of cuprous chloride should be precluded by the presence of steam, the green colour greatly predominates. Again, a small jet of hydrogen or steam impinging on a carbon-monoxide flame coloured intensely blue by cuprous chloride produces the green at the point of contact.

The remaining point of interest is to ascertain which of the oxides of copper produces the green colour. When carefully purified CuO is dusted on to a Bunsen-flame, a green tint is at once produced; and the deposit obtained on porcelain from the green part of a copper-chloride flame appears to be black at the instant of deposition. These facts point to cupric oxide as the substance which produces the green colour. On the other hand, cupric oxide is a substance which loses oxygen at a high temperature. The dissociation of cupric oxide was studied by Debray and Joannis (*Compt. Rend.* xcix. p. 583, 1884). Heated *in vacuo* they found it to yield oxygen at 350° C. At the melting-point of silver the tension of this oxygen amounted to 56 millim., and a little above the melting-point of gold to 1000 millim. It would appear to be impossible for cupric oxide to exist at the average temperature of a Bunsen-flame, for this would demand an oxygen-tension vastly greater than exists within or around such a flame. It seems therefore necessary to ascribe the green glow to cuprous oxide or some lower oxide of copper, but I have been unable after several attempts to volatilize cuprous oxide by external heating.

It has already been stated that a cuprous-chloride flame containing plenty of hydrochloric acid is surrounded by a dull red margin. This appears to be due to cupric chloride. When a super-aërated flame is obtained in the separator and is supplied with a spray of copper chloride, it is tinged wholly green and is surrounded by a green halo. Round such a flame the existence of cuprous chloride is impossible, and when a piece of asbestos, soaked in hydrochloric acid, is introduced into the halo we do not get as a matter of fact any blue colour, but the ruddy margin immediately appears, and it seems impossible to attribute this to anything but the formation of cupric chloride, which, in the presence of oxygen and hydrochloric acid, remains as such and gives the feeble red glow.

The behaviour of cupric chloride in the separator admits of easy explanation. In the inner cone the average temperature is extremely high, and the products there generated consist largely of carbon monoxide and free hydrogen. The cupric chloride will therefore not only lose its chlorine but the cuprous chloride, if we suppose it to be formed for a moment, will be immediately attacked by the reducing gases and lose the remainder of its chlorine. We have therefore metallic copper, and the average temperature is not sufficient to produce its characteristic spectrum. The copper and the hydrochloric acid resulting from the decomposition of the cupric chloride pass upwards. Some of the former is deposited as a thin metallic film on the inner walls of the outer tube. The rest passes to the outer cone where, at the lower average temperature and in contact with atmospheric oxygen, some cuprous oxide is formed and gives the green tint and oxide spectrum. At the same time some cuprous chloride is formed by the hydrochloric acid, and gives the faint traces of the chloride spectrum.

It is important to observe that, according to the above explanation, cupric chloride is decomposed in the inner cone without evincing any spectrum at all. The fact that the salt is easily reduced to cuprous chloride at a comparatively low temperature, and that cuprous chloride can itself be easily deprived of its chlorine by heating in a current of gases of the same composition as those that are passed into the separator, would lead one to the conclusion that the salt undergoes these changes before actually entering the inner cone. In this case we might at first expect to see some coloration below it, and, indeed, Gouy (*loc. cit.* p. 29) describes such an appearance, stating that a line of coloration is distinctly visible parallel to and within the cone. I have repeatedly tried to verify this observation, but could not succeed in doing so either by the eye or the spectroscope. The matter is, however, of no great consequence.

Flame-Spectrum of Gold Trichloride.

Owing to the easy decomposability of gold trichloride and the desirability of ascertaining more accurately the source of the spectrum commonly attributed to it, I have examined it with the separator.

When gold trichloride is introduced on the end of a platinum wire into a Bunsen-flame, a bright green flash of light is produced accompanied by some bright sparks. The coloration only lasts a very short time, and a considerable residue of metallic gold is left on the wire. These facts are noted and a map of the spectrum is given by Lecoq de Boisbaudran (*Spectres Lumineux*).

A moderately dilute solution of gold trichloride, introduced into the separated cones by means of the apparatus used for copper salts (p. 123), does not colour either of them; but when a piece of asbestos moistened with strong hydrochloric acid is held in the upper cone, a brilliant green colour is produced and the green lines are seen in the spectroscope. When the coal-gas is previously passed through the saturator containing asbestos moistened with strong hydrochloric acid, the outer cone becomes slightly green, especially at the edge. If, however, the saturator is jacketed with steam, so as to increase the volatilization of hydrochloric acid, the upper cone becomes intensely green. The same effect is obtained by using chloroform in the saturator.

If when, in either of the above ways, the upper cone has acquired a bright green colour, the outer tube of the separator is slid down over the inner one, the colour diminishes in intensity, and when ultimately the orifices of the two tubes are level, it disappears almost entirely except at the extreme edge. The only alteration which the outer cone can suffer by this approximation to the inner one is that its average temperature must increase, whence it appears that the coloration by the gold salt depends upon two circumstances—abundance of hydrochloric acid and a low average temperature.

This conclusion is easily confirmed. If, instead of bringing the cones nearer, the upper one be surrounded by oxygen instead of air, it becomes smaller and of higher average temperature, and its green colour disappears except at the extreme edges.

The fact that a chloride of gold can under any circumstances produce its individual spectrum is at first thought remarkable when we consider the extreme ease with which the salt is decomposed, and though the lower chloride or chlorides might be formed, they are likewise easily decomposed, leaving only metallic gold. There can be no doubt, indeed, that gold trichloride is decomposed completely at a temperature far below the average one of the flame in which it yields a spectrum. It has, however, been observed by Debray (*Compt. Rend.* lxix. p. 984, 1869) that gold chloride may be obtained at 300° by passing a current of chlorine through a tube containing the metal, from which it is evident that the salt may exist at abnormally high temperatures provided an excess of chlorine be present. To test this question further, I performed the following experiment.

By means of an electric current a pure gold wire was raised to bright redness in a tube partially exhausted of air. Chlorine was then allowed to enter the tube in considerable quantity. When this was done, a slight sublimate was immediately formed on the sides of the tube opposite to the glowing wire, and this sublimate on examination proved to be gold trichloride. From this it is apparent that in presence of abundance of chlorine, gold chloride may be formed at a red heat, and so emit its characteristic spectrum. The case is not an exception, but rather an example of the generalization that dissociable bodies become stable in presence of excess of one of the products of dissociation.

It is now easy to understand why gold chloride introduced into a flame on a platinum wire gives a spectrum. The great bulk of the salt is decomposed so as to give an atmosphere of chlorine in which a small portion of the salt volatilizes without decomposition. As has been already noted, much metallic gold remains on the wire.

I have shown that in using the separator the gold-chloride spectrum may be maintained by introducing abundance of hydrochloric acid or chloroform (the interconal gases contained no free chlorine), and that though the coloration may be for the most part quenched by making the flame hotter, it is most persistent at the edges. From these facts it appears that, so far as the formation and stability of gold chloride are concerned, an atmosphere of hydrochloric acid and oxygen is potentially one of chlorine, the stable arrangement of the system at a high temperature changing as follows [*] :—

$$3O_2, 12HCl, 4Au \quad \text{becomes} \quad 6H_2O, 4AuCl_3.$$

It is clear, therefore, that provided we have a sufficient quantity of hydrochloric acid or free chlorine, gold chloride may exist in a flame at a temperature sufficiently high to produce its spectrum.

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[*] It is stated in Gmelin's 'Handbook,' vi. p. 215, on the authority of Proust, that gold is soluble in hot hydrochloric acid in presence of air.

Salts of the Alkalis.

Salts of the alkalis (and, so far as I have examined them, of the alkaline earths), when introduced into the separator by means of the spray, impart their characteristic tint and spectrum to each cone, but as the inner cone has a much higher average temperature than the outer one it acquires by far the brighter tint.

These facts may be exhibited in a very striking way as follows:—A mixed solution of cupric chloride and lithium chloride is introduced into the sprayer feeding a separator with air; if the gas-supply be in excess, the undivided flame shows a mixed colour due to the copper and lithium salts; but if now the gas-supply be diminished and the cones allowed to separate, the inner cone appears bright crimson and the outer one only green. The explanation of this is very simple: the colour proper to the copper salt is, as we have seen, developed only in the outer cone, that due to the lithium salt in both cones; but in the upper one it is so faint as to be entirely masked by the green of the copper salt.

Conclusions.

The experiments recorded in this paper afford some evidence as to the validity of the view of the origin of flame-spectra advocated by Pringsheim. If, as he concludes, the flame-spectra commonly attributed to the alkali metals are a direct consequence of chemical processes occurring in the flame, the same is presumably true for the spectra of chemical compounds such as those of copper and gold. As a matter of fact chemical changes do accompany the production of the spectra dealt with in this paper. Thus when cupric chloride is introduced into the flame, we have the formation of cuprous chloride and of cuprous oxide. The case of gold chloride is more important. In the case of this salt the spectrum is only developed when a large excess of chlorine or of hydrochloric acid and air are present; in their absence a considerable quantity of a spray or dust of the salt may be passed through the flame without giving any spectrum. The gold chloride, in fact, can only be maintained at a temperature sufficient to develop its spectrum when it is surrounded by an atmosphere either of chlorine or of an equivalent mixture of hydrochloric acid and oxygen. The gold-chloride molecules, however, must not be regarded as remaining intact under these circumstances, for where a dissociable salt appears to be maintained in the undissociated state, through the presence of an excess of one of the products of dissociation, we ascribe it to the fact that, if momentarily dissociated, there is instantly a reunion. Whilst, therefore, on the one hand, the high temperature at which the gold-chloride spectrum is developed compels the separation of the gold and chlorine, the large excess of chlorine on the other hand, by the action of mass, compels a recombination. Though this in a sense is tantamount to saying that the gold-chloride molecules remain undissociated, the dynamical view of dissociation obliges us to picture a constant interchange between atoms of gold and atoms of chlorine.

We are obliged to conclude, therefore, that the experiments recorded above are quite in harmony with the view advocated by Pringsheim.

In a previous part of this paper I have offered some criticisms of the experiments on which Pringsheim based his conclusions. Notwithstanding this I have never considered his view to be disproved: on the contrary, it seems *prima facie* to be a reasonable explanation of many phenomena occurring in flames. The facts I have now brought forward are in harmony with it, but I believe the evidence is still far from complete, and that further experiments are necessary to establish the doctrine that the light-emission from coloured flames is a direct consequence of chemical processes.

I have to express my grateful acknowledgments to Sir G. G. Stokes, Bart., for the interest he has taken in the work recorded in this paper and for his invaluable and ever ready counsel. I have received much assistance from Mr. Frankland Dent, B.Sc., who especially has devoted the most patient labour to the drawing of the spectra.

The chief conclusions arrived at in this part of the paper are:—

I. When cupric chloride is introduced into a flame, three substances are formed: metallic copper, cuprous chloride, and cuprous oxide. The first of these give a bright yellow flame and a continuous spectrum; the second a bright blue tint and brilliant spectrum of bands and lines; the last a green tint and spectrum of not very strongly developed bands. Under certain circumstances cupric chloride may exist in a flame, when it gives a feeble ruddy tint and a continuous spectrum.

II. Gold chloride gives a flame-spectrum only in presence of an excess of chlorine or of hydrochloric acid and oxygen.

III. In the above cases the development of a spectrum is concomitant with chemical changes affecting the substance concerned; a fact in harmony with the view as to the origin of flame-spectra advocated by Pringsheim.

IX. *Specific Inductive Capacities of Water, Alcohol, &c.*

By J. Hopkinson[*].

IN the December number of the Philosophical Magazine is a short article by Prof. R. A. Fessenden on the Measurement of the Specific Inductive Capacities of Water, Alcohol, &c. In this article he states that the high values found by Cohn and Arons and others for water, alcohol, &c. are not correct, but that the true values are in every one of these substances very nearly equal to that called for by Maxwell's theory. He also states that all the determinations of such substances as sulphur, &c. are incorrect. The observations said to be incorrect are not those of a single observer, but of many whose results are in good accord.

Taking solids first, it has been shown that the capacity of light flint-glass at ordinary temperatures is the same whether the time of charge is $\frac{1}{20,000}$ second, or $\frac{1}{2}$ second, that it is independent of the potential of the charge, and that its value is about 6·7[†]. It is also well known that this glass insulates so well that it will hold its charge for months[‡]. Is it suggested that these results are vitiated by electrolytic polarization or by a hypothetical laminated structure of the material? The specific inductive capacity of ice has been determined by Bonty[§]. He finds 78, practically the same value as Cohn and Arons find for water. But the resistance is from 10^5 to 10^6 times as great as that of water, which quite precludes the suggestion of electrolytic polarization.

Turning to liquids, we have a large number of determinations which also deviate from Maxwell's law. Take, for example, castor-oil and ether. Both insulate well enough to make certain that electrolytic polarization does not affect the result. Quincke determined the capacity of ether[||] by three very different methods and found it in each case about 4·7; my result by a fourth method was 4·75. For castor-oil I obtained by two very different methods 4·78 and 4·82[¶]. All these results deviate much from Maxwell's law making use of refractive indices for visible rays, and render the results of Cohn and Arons and the independent results of Tereschin for water not improbable *à priori*. Indeed, I think much more evidence will be needed than Prof. Fessenden has given before they are doubted.

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[*] Communicated by the Author.

[†] Phil. Trans. vol. clxxii. p. 372, and Gray's 'Absolute Measurement in Electricity and Magnetism,' vol. i. p. 473.

[‡] Phil. Trans. vol. clxvii. p. 610.

[§] *Comptes Rendus*, p. 533, March 7, 1892.

[||] Gray, p. 483.

[¶] Phil. Trans. (*loc. cit.*), and Proc. Roy. Soc. October 1887.

Prof. Fessenden also states that pure water insulates as well as indiarubber! The highest recorded resistance for water is far below that of indiarubber.

I would not have troubled you with this note were it not that anything appearing in the Philosophical Magazine carries authority, and if inaccurate is calculated to mislead.

X. *On* Colonel Hime's '*Outlines of Quaternions.*'

To the Editors of the Philosophical Magazine.

GENTLEMEN,

I CANNOT agree with your reviewer in holding that paragraph 11 of the 'Outlines' is not quaternions. The equation

$$i=j=k=\sqrt{-1}=-i=-j=-k,$$

as your reviewer says, may be nonsense; nevertheless it follows from the fundamental principles of quaternions as laid down by Hamilton and Tait. It is said that $i^2=-1$ and $j^2=-1$; therefore it follows that $i^2=j^2$, unless in quaternions the axiom does not hold which says that things which are equal to the same thing are equal to one another. But from $i^2=j^2$ it follows that $i=+j$ or $-j$, for we are told that it is only the commutative law of all the laws of algebra which breaks down, and here that peculiarity does not enter. By extending the same reasoning to the other two pairs, we obtain

$$i=j=k=\sqrt{-1}=-i=-j=-k.$$

How does your reviewer demonstrate that it is nonsense? He says that i, j, k have already been defined as co-perpendicular unit-vectors, and to say that they are equal is to rob them arbitrarily of their most characteristic feature, so that they are no longer what they were defined to be. Yet a few sentences before this same writer defends Hamilton's no less arbitrary violation of the definition of a vector, which does not indeed rob it of any of its meaning, but piles on it what does not belong to it. That which in Hamilton is an "outburst of genius" is in Colonel Hime "contrary to the whole genius of common sense."

The manner in which the author founds the calculus is not satisfactory to your reviewer. This is not surprising; on examination I find that it is based on a collection of definitions. The fundamental rules are explained as follows:—In ij the former symbol is a quadrantal versor and the latter a vector, the effect of the former on the latter is to change it into k. Logically, we expect that in ii the former symbol is a quadrantal versor and the latter a vector, giving i as the result; but it is not so: both symbols are now to be considered quadrantal versors, giving $i^2 = -1$. These two inconsistent theories are simultaneously applied to find the product of two vectors,

$$m_1 i + m_2 j + m_3 k \text{ and } n_1 i + n_2 j + n_3 k.$$

The product consists of two kinds of terms; $m_1 n_1 ii$ is a type of the one, and $m_1 n_2 ij$ of the other. We are asked to believe that in $m_1 n_1 ii$ both unit-vectors become quadrantal versors, while in $m_1 n_2 ij$ it is only the former of the two. The operator and operand theory is applied to one set of terms, and a double operator theory to the other set of terms; while in the vectors themselves there is no operator at all.

In my papers on Space-analysis I have attempted to lay down the fundamental principles in a logical manner. When that is done, the meaning of every expression and equation becomes clear, and there is no need for a special chapter such as we find in the 'Outlines,' on the "Interpretation of Quaternion Expressions." The best proof of the correctness of my principles is that they have enabled me to carry the analysis beyond the point where Hamilton left it.

In conclusion I wish to say that I yield to no one in admiration of the works of Hamilton and Tait. The attitude of mind of your reviewer appears to be that of "wondering awe." In that I cannot follow him; I stand in awe of the truth only.

ALEXANDER MACFARLANE.

Ithaca, N. Y.

XI. *Notices respecting New Books.*

An Introduction to Physical Measurements, with Appendices on Absolute Electrical Measurement, &c. By Prof. F. KOHLRAUSCH. *Third English edition, translated from the Seventh German edition, by* T. H. WALLER, *B.A., B.Sc., and* H. R. PROCTER, *F.I.C., F.C.S.* London: J. and A. Churchill, 1894.

SOME time ago reference was made in these pages (Phil. Mag. [5] vol. xxxvii. pp. 334, 502) to the fact that the earlier editions of this work had become somewhat out of date by reason of the widening of the scope of physical measurements. Prof. Kohlrausch very rightly pointed out that the fault did not lie on his side, as the latest (seventh) German edition contained a very large amount of new matter. This edition now becomes accessible to us in the form of an English translation.

Prof. Kohlrausch has aimed at giving a tolerably comprehensive list of experiments which may be performed in a physical laboratory, as exercises for students or as parts of a physical research. This wideness of aim necessarily entails a certain amount of brevity of description, and consequently details of apparatus are generally omitted. The book differs in this respect from others of its class, the majority of which are either intended to meet the wants of special students or else have been compiled primarily for use in some particular laboratory: in either case the details referring to construction or arrangement of apparatus are often found inapplicable when the book comes to be used under other conditions. Prof. Kohlrausch has omitted mere lecture-experiments and such as are designed to establish the truth of physical laws: it is assumed in all cases that the experiment is undertaken to determine some physical constant. The omission of the determination of coefficients of absolute expansion of liquids by heat, and the measurement of wave-lengths by the biprism, may be due to this cause, although the former are often required in physical work. A more important defect is the absence of all reference to the measurement of latent heat, either of fusion or vaporization. In connexion with electricity and magnetism the number of experiments which might be described is now so great that a selection becomes necessary, and in the present volume the choice has been on the whole a good one. The only measurement which does not receive attention is that of the mutual induction between a pair of coils, no method being given for its determination. In describing the various forms of galvanometer the D'Arsonval or suspended coil type ought to have been included; and in connexion with Mance's method for the measurement of battery resistance the use of a condenser with the galvanometer (Lodge, Phil. Mag. June 1877) should be referred to. It does not seem to be generally known that satisfactory results can be secured by this simple device. In the appendix on the absolute system of measurements the dimensions of dielectric capacity and magnetic permeability are each given as zero, with the result that the same quantities appear to be of different dimensions according as they are measured in electrostatic or electromagnetic units.

The translators have given a fair rendering of the German text, but unfortunately they have retained nearly all the misprints of the original. This is the more remarkable seeing that a printed list of corrigenda exists, and has been issued with (at any rate, some) copies of the German edition. Out of this list of fifteen misprints only three are corrected in the present translation. Several additional ones have been introduced, the most unfortunate of which is the use of the word "density" for "specific gravity" on p. 44, just in the place where a distinction is being drawn between the two terms. In the tables at the end of the work a few minor omissions and misprints occur; for example, in Tables 30, 32, and 33 the units of measurement are not stated, while in Tables 22 and 22(*a*) C.M.G. is printed for C.G.S. The symbols used by Prof. Kohlrausch have generally been retained, especially in the sections dealing with electricity, where the use of *i* for current-strength and *w* for resistance will scarcely commend itself to English readers. On the other hand, Kohlrausch's *n* for refractive index has been replaced by μ, in accordance with English usage. The volume forms an important addition to the literature of the physical laboratory, and can easily be cleared of such superficial blemishes as have been indicated. JAMES L. HOWARD.

Watts' Dictionary of Chemistry.

Watts' Dictionary of Chemistry; revised and entirely rewritten. By M. M. PATTISON MUIR, *M.A.*, *and* H. FORSTER MORLEY, *M.A. Assisted by eminent Contributors.* In four volumes. Vol. IV. London: Longmans, Green, & Co., 1894.

THIS fourth and concluding volume of the well-known chemical dictionary brings to a close a standard work of reference of which the first volume appeared in 1888. Altogether we shall not be far wrong in stating that the editors have taken about a decade in revising, rewriting, compiling, and editing the vast amount of material which constitutes the modern science of Chemistry. That they have done their task well has already been acknowledged in noticing the former volumes in the pages of this Magazine. It is with great satisfaction that we are enabled to renew this acknowledgment in the case of the present volume, which extends to 922 pages and contains an Appendix of 34 pages comprising the more noteworthy of the recent discoveries in inorganic chemistry.

A dictionary of science is not an easy work to treat of from a reviewer's point of view. But in this fourth volume there are certain long articles on special subjects by well-known authorities, which form a most valuable feature of the work, and to which attention may be directed. Thus, instead of the separate articles on electricity, light, heat, &c., which appeared in the old dictionary, we have one comprehensive article on Physical Methods used in Chemistry, which occupies no less than 100 pages and is divided into the fourteen sections:—Capillarity, Crystallographic Methods (references only), Dialysis and Diffusion, Dynamical Methods (references only), Electrical Methods, Freezing-points of Solutions (references only), Optical Methods, Osmotic Pressure (references only), Photographic Methods (references only), Specific Heats of Solids (references only), Thermal Methods, Vapour Pressures of Solutions (references only), Viscosity of Liquids, Volume Changes (references only). In cases where references only are given, it is because the section forms the subject of a special article elsewhere in the work. As a guarantee of soundness of treatment we need only mention the names of the contributors. Thus, Prof. Ostwald is responsible for the section on electrical methods (46 pages), Prof. Hartley writes on optical methods (spectroscopic methods), Mr. George Gladstone the section on refraction and dispersion, and the editor (Mr. Muir) on polariscopic methods. Dr. Capstick contributes the sections on capillarity and viscosity. The section on thermal methods is also written by Mr. Muir. Taking it as a whole this article on Physical Methods is perhaps one of the most valuable in the Dictionary; with the references and the original communications it constitutes a compact little monograph on Physical Chemistry, and those who have followed the developments of science since the time of the old Watts' Dictionary, cannot but be struck by the vast encroachment of Physics upon Chemistry, to the great advantage of both sciences.

The article on Photographic Chemistry is by Prof. Meldola and is compressed into about 5 pages; Dr. Halliburton contributes 15 pages of most valuable information on Proteids; Mr. O'Sullivan writes on Starch, and also a long article (35 pages) on Sugar, in which the enormous development in this branch of organic chemistry, due chiefly to the researches of Emil Fischer, is very well summarized and set forth. The article on Solutions is divided into two sections—the first, by Prof. Arrhenius, representing the views of those who hold to the physical theory, and the second, by Prof. S. U. Pickering as the representative of the so-called "hydrate" theory. It is interesting to compare the views of the two authors. Arrhenius sets out with the definition:—"A solution is a homogeneous mixture of two or more bodies in the liquid state." Pickering states:—"The view that hydrates exist in aqueous solutions, and analogous compounds in non-aqueous solutions, is one that has long been held by many chemists; it is only in the last few years, however, that the hydrate or association theory has assumed a precise form, and that definite experimental evidence in support of it has been accumulated." It is most valuable to have the views of the supporters of the two rival hypotheses thus brought into juxtaposition, and the editors have shown great judgment in inviting contributions from both schools in the present unsettled state of this most important subject.

Among other special articles attention may be called to that on Specific Volumes by Prof. Thorpe, and that on Terpenes by Prof. Tilden. The latter gives in a space of some 11 pages a very good *résumé* of our present knowledge of the compounds of this group, and here again one cannot fail to be struck with the great development of chemical science since the publication of the old dictionary. It is chiefly to the work of Wallach, and to the introduction of the conception of the asymmetric carbon atom, that this advancement is due.

The various short articles by the editors do not call for special notice; it is sufficient to state that the standard of excellence has been maintained throughout. It is with the greatest pleasure that we acknowledge the indebtedness of the whole chemical world to the editors of this great work and their coadjutors. The selection of contributors has from the beginning been most judicious, the treatment of the various subjects has been kept well within the bounds of sound knowledge, and the terseness of description has enabled them to compress into the allotted compass of four volumes the vast mass of fact and theory of which the modern science of Chemistry is composed. It is a matter for congratulation that English scientific literature is in possession of such a work. To simply commend it to the notice of chemists is insufficient; we may go so far as to declare that it is absolutely indispensable to every worker in every department of our science.

XII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xxxviii. p. 577.]

November 7th, 1894.—Dr. Henry Woodward, F.R.S., President, in the Chair.

THE following communications were read :—

1. 'Notes on some recent Sections in the Malvern Hills.' By Prof. A. H. Green, M.A., F.R.S., F.G.S.

The sections described occur on the east side of the Herefordshire Beacon, and for convenience are named the Warren House Rocks. They are bedded, and have a general north-and-south strike. The great bulk of the rocks are hard, close-grained, and splintery, and are largely altered, and in many cases thickly veined with calcite.

Details of their structure are given; and the author states that he is inclined to regard them as a group of bedded acid lavas and tuffs, crossed by three bands of dolerite. What little balance of evidence there is seems to be in favour of the intrusive character of the dolerites. No true limestones have been found, and the only very calcareous rock seen is regarded as a rock belonging to the volcanic group which has been largely calcified.

Somewhat similar rocks are found on the southern part of Raggedstone Hill, and a shattered felstone occurs forming an isolated boss south of Chase End Hill.

Several hypotheses present themselves as to the relationship between the Warren House Rocks and the Crystalline Schists. The former may be distinct from the latter, in which case the absence of mechanical deformation would indicate that they are younger. If we consider that the Malvern Schists have been formed out of volcanic rocks by dynamic metamorphism, the Raggedstone Hill rocks may be a portion of the volcanic complex which has undergone only partial transformation, whilst the Warren Hill rocks have altogether escaped metamorphism, the crystalline schists representing its final stages.

2. 'The Denbighshire Series of South Denbighshire.' By Philip Lake, Esq., M.A., F.G.S.

The area to which this paper chiefly refers is the south-western quarter of the Llangollen basin of Silurian rocks. The beds are here very little disturbed, and the sequence is readily made out. The following subdivisions are recognized (in descending order):—

Leintwardinensis-slates; with *Monograptus leintwardinensis.*
Upper gritty beds; with no fossils known.
Nantglyn flags; with *M. colonus, Cardiola*, &c.
Moel Ferna slates; with *M. priodon, M. Flemingii.*
Pen-y-glog grit.
Pen-y-glog slate; with *M. personatus, M. priodon, Retiolites Geinitzianus*, &c.

Farther east the fossiliferous beds of Dinas Brân appear to lie considerably above the *Leintwardinensis*-slates.

On comparison with other areas it is found that this succession is almost identical with that in the Long Mountain, in North Denbighshire, and in the Lake District. It is also inferred that the *Leintwardinensis*-slates represent the Leintwardine Flags of Herefordshire, and that the Dinas Brân beds correspond with a part of the Upper Ludlow.

3. 'On some Points in the Geology of the Harlech Area.' By the Rev. J. F. Blake, M.A., F.G.S.

In testing the conclusions arrived at in regard to the Llanberis and Penrhyn area by an examination of that of Harlech, two questions are raised concerning the latter:—(1) Can a succession be traced below the Purple Slates similar to that which the author has described as occurring in Caernarvonshire? and (2) Where is the most natural break in the series, and does it show an unconformity?

With reference to the first question, the author gives his reasons for concluding that, as far as the succession is seen in the Harlech area, it is similar to that of Caernarvonshire. A group of Purple Slates is described which so closely resembles the Llanberis and Penrhyn Slates that he considered himself justified in definitely correlating them with those slates. Below these are slaty greywackes, which, if not identical with those of Caernarvonshire, bear a greater resemblance to them than any other part of the series does. No older beds are seen. Above the Purple Slates are the Harlech Grits proper.

In discussing the second question, the author describes conglomeratic beds occurring some distance above the base of these Harlech Grits; but at Pont Llyn-y-Crom the junction between them and the underlying Purple Slates shows features recalling what is seen at Bronllwyd. He discusses the possible existence of an unconformity at the base of these grits, and concludes that on the whole the phenomena point, though not very strongly, to an unconformity of no great importance.

The concluding part of the paper is occupied with a consideration of the question of classification of the Cambrian strata and those in juxtaposition with them.

XIII. *Intelligence and Miscellaneous Articles.*

ON THE VELOCITY OF SOUND IN GASES.

To the Editors of the Philosophical Magazine.

GENTLEMEN,

I READ in No. 232, September 1894, of the Philosophical Magazine a paper by Mr. Webster Low, "On the Velocity of Sound in Air, Gases, and Vapours for Pure Notes of different Pitch." I deem it important to acquaint the Editors of the Philosophical Magazine that as long ago as 1881 I used a method nearly identical with Mr. Low's in order to determine the velocity of sound in some gases (air, CO_2, N_2O), and particularly in *chlorine*, its value for this gas being till that time quite unknown. My results were published in the Acts of the Venetian Institute[*], and in abstract in other periodicals[†]. As to chlorine, which was the gas that interested me the most, I found at 0°

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[*] *Atti del R. Istituto Veneto di Scienze, Lettere ed Arti*, serie 5, vol. viii. p. 494, and serie 7, vol. iv. p. 1113.

[†] *Journal de Physique théorique et appliquée*, vol. x. p. 410 (1881); *Beiblätter zu den Annalen der Physik und Chemie*, vol. v. p. 564 (1881).

$$v = 206{\cdot}4 \text{ metre,}$$

and

$$k = 1{\cdot}327.$$

Some months later Mr. Strocker found for chlorine with a method quite different from my own,

$$v = 205{\cdot}3 \text{ metre,}$$

$$k = 1{\cdot}323.$$

With my best thanks,

I am,
Respectfully yours,
TITO MARTINI.

Venice, November 20, 1894.

INFLUENCE OF MAGNETIC FIELDS ON THE ELECTRICAL CONDUCTIVITY OF BISMUTH.

To the Editors of the Philosophical Magazine.

GENTLEMEN,

I regret that mention of the papers by Dr. Edm. van Aubel in the *Annales de Chimie et de Physique* for 1889, and in the *Journal de Physique* for 1893, was omitted from my paper "On the Influence of Magnetic Fields on the Electrical Conductivity of Bismuth" in your Magazine for November last. In his work on the Temperature-Coefficient of Bismuth, van Aubel found that it was considerably changed in a magnetic field; and at the "Congrès des Électriciens" in Paris in 1889 he emphasized the necessity for observing the temperature, in measuring magnetic fields by the resistance of bismuth spirals.

I remain, Gentlemen,
Yours faithfully,
JAMES B. HENDERSON.

The Yorkshire College, Leeds.

ON THE INFLUENCE OF TEMPERATURE ON THE SPECIFIC HEAT OF ANILINE. BY E. H. GRIFFITHS, M.A.

NOTE, *Dec.* 7, 1894.—In a communication made to the Royal Society on November 22, Professor Schuster pointed out an error in my determination of the value of J, viz. that I had not made a necessary correction for the specific heat of the air displaced by the water; for the method I had adopted gave the difference in the rate of rise when a certain space was filled first with air and then with water. This correction raises my value of J by about 1 in 4000.

Now the specific gravity of aniline (1·02) but slightly exceeds that of water; and as the method described in the preceding pages also depends upon the measurement of differences in the rate of rise, the correction would eliminate and would, therefore, not affect the values of the specific heat of aniline as given in Table VII. Again, if there are any errors in the values of the electrical standards upon which my determination of J depends, they also would eliminate during the calculations by which the specific heat of aniline was ascertained. There can, therefore, be no doubt that the value assumed for J ($4{\cdot}198 \times 10^7$) is the correct one to be used for the reduction of the observations on aniline.

ON THE DIELECTRIC POWER OF ICE. BY M. A. PEROT.

I published on June 29, 1894, the result of experiments made to determine the dielectric constant of ice by electrical oscillations. In calculating these experiments, which I had carried out as for glass, I made an error due to the external capacity, which in those experiments is altered, the condenser being wholly or partially immersed in the dielectric. M. Blondlot having pointed out the disagreement between his results and those which I had obtained, I have gone through the calculations, and made new experiments, the result of which is given below:—

λ (air).	λ_1(ice).	$\sqrt{K}$.
91	130	1·43
91	133	1·46
136	186	1·37
136	197	1·44
151	215	1·42
149	214	1·44

$$\text{Mean } \sqrt{K}=1{\cdot}43\,;\ K=2{\cdot}04.$$

—*Comptes Rendus*, October 8, 1894.

ON THE REFRACTION AND DISPERSION OF ELECTRICAL RAYS. BY E. GARBASSO AND E. ASCHKINASS.

The authors summarize the results of their research as follows:—

We have shown that the rays proceeding from a Hertz's primary conductor may, by means of a prism built up of resonators, be resolved into a spectrum, and draw from this the following conclusions:—

(*a*) The rays of electrical force emitted are not necessarily to be regarded physically as monochromatic, but as compound, with as much justification as ordinary light.

(*b*) Helmholtz's theory of colour-dispersion acquires fresh support from our experiments.—Wiedemann's *Annalen*, No. 11, 1894.

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[FIFTH SERIES.]

FEBRUARY 1895.

XIV. *Comparative Review of some Dynamical Theories of Gravitation.* *By* Dr. S. TOLVER PRESTON*.

Introduction.

THE modes of accounting for natural phenomena have been very different at different times. The old philosophers had in general scarcely an idea of that which we now call a mechanical explanation; they figured to themselves rather the agencies working in nature as living beings. This applies also to Kepler, who banished from himself any idea of a mechanical explanation of the laws discovered by him. On the basis of the researches of Galileo, Newton was the founder of the Mechanics of to-day; and on his principles the edifice of the action-at-a-distance theory has been founded. Until Newton's time the notion of a direct action at a distance was completely unknown: on the contrary, many experiments exist by the Greek philosophers to account for the seeming action at a distance by the intervention of a medium; therefore Demokritos sought to explain natural phenomena by the motions of very fine bodies. First Boscovich, Mosotti, Wilhelm Weber, and many others developed the aspect of nature on the basis laid down by Newton, in accordance with which the universe consists of a number (if even very great) of material points, which, without anything intervening, act on each other directly at a distance, according to a mathematically exact formulated law. If the initial positions and velocities of all the atoms are given, then their motions can be calculated for any periods of time from the equations formulated by Newton, and so a clearly defined mathematical problem is presented.

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* Being a Dissertation presented to the Philosophical Faculty of the University of Munich, for the attainment of the degree of Doctor of Philosophy (translated from the German). Communicated by the Author

It is, however, well to observe that Newton did not believe in such an action at a distance without the intervention of something, as appears from his third letter to Bentley, where he says:—

"That gravity should be innate, inherent, and essential to matter, so that one body may act upon another at a distance through a *vacuum*, without the mediation of anything else, by and through which their action and force may be conveyed from one to another, is to me so great an absurdity, that I believe no man who has in philosophical matters a competent faculty of thinking, can ever fall into it" (Newton's third letter to Bentley, February 25, 1692–3).

In the same sense speak many subsequent important scientists. For instance Count Rumford remarks:—

"Nobody surely in his sober senses has ever pretended to understand the mechanism of gravitation, and yet what sublime discoveries has our immortal Newton been enabled to make, merely by the investigation of the laws of its action" ("An Inquiry concerning the Source of the Heat which is excited by Friction," by Count Rumford, Phil. Trans. 1798).

These last scientists are therefore not satisfied with the Boscovich-Mosotti explanation of natural phenomena; they demand rather an explanation (by the intervention of a medium) of the seeming action at a distance. To give such an explanation was never seriously attempted by Newton: the first attempt of that kind is to be found in the mechanical gravitation theory of Le Sage, born at Geneva in 1724. This theory is contained in a memoir published in the Transactions of the Royal Berlin Academy for 1782, under the title *Lucrèce Newtonien.* There is also a book, *Deux Traités de Physique mécanique*, edited by Pierre Prévost, Paris, 1818, which contains a full description of Le Sage's theory.

Le Sage lays emphasis on the probability of the existence of a mechanism of gravitation, and devoted his life to the development of his idea. The introductory paragraph of his memoir (entitled *Lucrèce Newtonien*) is as follows, translated from the French original, viz.:—

"I propose to show that if the first Epicureans had had as healthy ideas of Cosmography as several of their contemporaries (to whom they would not listen), and only a part of the knowledge of Geometry which was then prevalent, they would in all probability have discovered the laws of universal gravitation and its mechanical cause. *Laws*, the discovery and the demonstration of which constitute the fame of the most powerful genius that has ever existed ; and *Cause*, which after having been the ambition for a long time of the greatest scientists, is at present the despair of their successors. So that, for example, the celebrated laws of Kepler, discovered somewhat less than 200 years ago, partly by gratuitous conjectures, and partly by repeated trial and error, would have been no more than inevitable corollaries which could have been arrived at by these ancient philosophers by investigating the mechanism of nature. The same conclusion applies also to the laws of Galileo upon the fall of bodies, the discovery of which took place still later, and which have been more contested, because the experiments upon which this discovery was based permitted a latitude in their results (necessarily rough), which would make them fit equally well with other laws, so that one did not fail to contest them : whereas the inferred consequences of the shock of atoms would have been unmistakably in favour of the only true principle, viz., equal accelerations in equal times." (Trans. of Royal Berlin Academy, 1782.)

On this paragraph the following opinion is emitted by Lord Kelvin, viz. :—

"If Le Sage had but excepted Kepler's third law, it must be admitted that his case, as stated above, would have been thoroughly established by the arguments of his "mémoire"; for the Epicurean assumption of parallelism adopted to suit the false idea of the earth being flat, prevented the discovery of the law of the inverse square of the distance, which the mathematicians of that day were quite competent to make, if the hypothesis of atoms moving in all directions through space, and rarely coming into collision with one another, had been set before them, with the problem of determining the force with which the impacts would press together two spherical bodies, such as the earth and moon were held to be by some of the contemporary philosophers to whom the Epicureans "would not listen." But nothing less than direct observation, proving Kepler's third law—Galileo's experiment on bodies falling from the tower of Pisa, Boyle's guinea-and-feather experiment, and Newton's experiment of the vibrations of pendulums composed of different kinds of substance—could either give the idea that gravity is proportional to mass, or prove that it is so to a high degree of accuracy for large bodies and small bodies, and for bodies of different kinds of substance" (Phil Mag. May 1873, p. 323).

Le Sage's *Theory*.

Le Sage based his theory on perfectly arbitrary assumptions. He assumed (*Deux Traités de Physique mécanique*, Paris 1818, edition Pierre Prévost) :—

(1) That a number of streams of atoms, equally distributed in space, exist; of which each stream moves continually in one and the same direction.

(2) The length of these streams (at the centre of which the universe known to us is placed) is finite, but very great; therefore gravitation must have a correspondingly limited period for existence.

(3) That the streams must be everywhere equally dense.

(4) That the mean velocity of the streams is everywhere the same.

The conditions above set forth depend manifestly on perfectly arbitrary assumptions, and it is not easy to see by what mechanism such streams should either originate or be kept up. As regards the behaviour of these streams of atoms towards gross matter, Le Sage assumes the following. Gross matter is chiefly freely penetrated by the streams of atoms, only a small part of their energy is absorbed by gross matter, which implies a continuous annihilation of energy. Whence it arises that every portion of gross matter opposes a certain shelter to every other neighbouring portion from the encounters of the streams of atoms; and from this the apparent attraction of the gross matter according to the Newtonian law of gravity is easily explained.

Lord Kelvin presupposes exactly the same streams of atoms as Le Sage; the mechanism which regulates or maintains these atom-streams therefore remains with him as obscure as with Le Sage. An important progress in Lord Kelvin's case consists, however, in the fact that he regards the atoms as elastic. In order to explain the elasticity, he proposes to regard the atoms as vortex rings in a perfect liquid. The elasticity of these is then explained by the laws which Helmholtz found to apply to the motions of such vortex rings.

The æther atoms then rebound from gross matter in accordance with the laws of elastic collision: instead of the absorption (annihilation) of energy assumed by Le Sage, Lord Kelvin supposes that the æther atoms, in addition to their translatory energy, also possess an energy of internal motion, just as Clausius assumes for the molecules of ordinary gases.

On account of the relatively very large dimensions and superior elastic rigidity of the gross molecule, it is scarcely disturbed by the collision of the very minute atom. On the other hand, the minute atom is thrown into strong vibration and rotation by the blow. This vibration or rotation ("internal motion") cannot evidently be generated out of nothing. The small atom therefore loses at impact a portion of its translatory motion, by converting the same into internal motion (vibration and rotation). The diminution of the translatory motion of the small gravity-atoms at their encounter with gross molecules is therefore rather to be looked upon as a necessary deduction than as an hypothesis. One might, indeed, easily illustrate this fact experimentally.

If an elementary example be excused, we can consider the case when any small elastic body such as a small polished steel key-ring is thrown against the surface of a polished steel anvil. A key-ring and an anvil (of the same metal) may be equally elastic, but on account of the considerable difference in their dimensions—therefore pliability—only the small ring will be thrown into perceptible vibration by the encounter (or into *rotation*, for the anvil cannot rotate on account of its mass). The ring rebounds with a diminution of its translatory motion, by converting the same into vibration and rotation.

The atom gains its full translatory motion gradually again by collisions against atoms of its own kind,—from the fact that the proportionality existing between the amount of translatory motion and the amount of internal motion of the atom continually strives to maintain itself constant; which is a known consequence of the kinetic theory of gases, demonstrated by Clausius.

So is explained how the æther atoms, in being sifted through gross matter, on the average lose a certain velocity of translatory motion, and that therefore a portion of gross matter "shelters" any other neighbouring portion from the impacts of the æther atoms.

The penetration of the two masses by the flying æther atoms brings about the fact that on the adjacent sides of the two masses the pressure of the medium is smaller than on the remote sides of the molecular surfaces of the two masses. The remote sides encounter the full or undiminished translatory velocity of the atoms. Therefore the two masses are naturally driven together, and with a force which obviously, from the nature of the case, must be proportional to the square of the distance of the masses. The further explanation of the gravitation effect is then exactly as by Le Sage's theory.

The present writer attempted in some papers, of which the first appeared in the Philosophical Magazine, Sept. 1877, to replace the arbitrarily assumed atom streams of Le Sage and Lord Kelvin by a motion which is exactly analogous to that which belongs to the kinetic theory of gases.

In that way the most obscure assumption of Le Sage's theory finds an unforced explanation—namely, how the symmetrical motion of the atoms under the continual changes of their direction produced by their collisions against gross matter, is *kept up*.

Now it has already been mathematically demonstrated in the case of ordinary gases, that an automatic correction goes on in a system of bodies or particles in free collision, and such a one that the particles are forced to move *equally* in all directions: and this is the absolutely necessary condition for equal pressure in all directions. The rate of establishment of this automatic correction, which is chiefly brought about by the oblique encounters, has, in fact, been calculated mathematically by Prof. Ludwig Boltzmann for ordinary gases. This adjustment (or correction) is in fact of such a stable character, that if the motion of the gas *particles* were artificially disturbed, the particles would of themselves equalize the motion again, so that an equal number of particles are moving in any two opposite directions. The motion can also be described so, that if we think of any small point situated anywhere in space, the atoms are at every instant flying towards and from this point, exactly as if it were a luminous point.

Hence it follows that when a system of atoms is left to itself, it will, by the principles of dynamics, automatically adjust the character of its motion in such a way that this motion is adapted to produce the gravitation effects. The motion of streams of atoms equally at all angles, which Le Sage gave forth as an arbitrary postulate, is attainable in a gas without any postulate. Instead of streams, each of which for itself maintains a constant direction of motion, and which cease to flow after a long epoch of time, we have a permanent motion of atoms correcting itself in a self-acting manner; and which fulfils the wished-for object.

So, therefore, we have succeeded, by starting from a very simple and thoroughly natural foundation, in establishing all those conditions which Le Sage needs for his theory.

Nevertheless there are certain assumptions concerning quantitative relations to be added. In the first place, the mean length of path of an æther atom must be assumed to be exceedingly great. If, namely, the same were small in proportion to the distance between two influencing masses, then in the intervening space between these masses, by the collisions of the æther atoms among themselves, the normal proportionality between translatory and internal motion of the atoms would be nearly restored (by encounters), and therefore the mutual shelter of the two masses would nearly be nullified.

The range of gravitation (its sphere of action) is therefore conditioned by the mean length of path of the atoms, and this may be regarded as an interesting deduction from the theory. Accordingly, on the assumption that the mean distances of the stars (excepting, of course, the relatively approximated double stars) are large in proportion to the mean length of path of the atoms, the inference would follow that the stars do not gravitate towards each other—and apparently in that way the universe would rather gain than lose in stability. One sees then that the mean length of path of the æther atoms must be great in comparison with those distances across which Newton's law has been demonstrated to apply with exactness.

In an article in the *Encyc. Brit.* 1875 (or Scientific Papers, vol. ii. p. 476) Maxwell raises the objection that by the atomic encounters gross matter would be raised to a white heat; he grounds this inference on the theorem that for thermal equilibrium between atoms or molecules the mean energy of translatory motion must be equal. Now the pressure (to take some symbol) is equal to the product of the mean energy of translatory motion L of an atom into the number N of atoms contained in the unit of volume. If, therefore, the mean energy of translatory motion of an æther atom be equal to that of a molecule of gross matter, which we can calculate in the case of ordinary gases, then N for the æther must have an enormous value, in order to be able to account for the gravitation pressure. Now Maxwell says: we are tolerably certain that N for the æther is small compared with the value of N for gross matter. From this he concludes that in order to explain the gravitation pressure, it is necessary to assume L enormously great. And according to the theorem that for thermal equilibrium L must be the same for all atoms (or molecules), it would follow that L also for the molecules of gross matter must finally assume a value which is much greater than that which we find in the case of gases. In other words, that all gross matter must be raised to a white heat by the collisions of the æther atoms. But, independently of the fact that the above-named theorem, relating to thermal equilibrium, for molecules or atoms of very different size is still contested, it seems to me that no cogent reason exists for the assumption that N is smaller for the æther than for gross matter. One can, in fact, imagine the æther atoms as small as one pleases;

then an enormous number of them can exist in the unit of volume combined with an enormously great length of path.

In general, in putting forward a theory of this kind, we should see no improbability in the assumption of either a very great or a very small number. Our objection to uncommonly great or uncommonly small numbers rests in fact upon custom, and regularly disappears as soon as the theory in question has further introduced itself.

There exists in space field enough, when necessary, for finer material, as our conceptions are not limited in the direction of smallness, and the smaller the particles, the quicker is their natural speed of motion, and the more intense the enclosed store of concealed energy: also the whole arrangement becomes all the less appreciable by our senses. The effects—called gravitational effects—on the other hand, do not escape detection by our senses; and reasoning from these effects, we trace and infer the invisible causes which lie at the basis of these effects.

Evidently there exists just as little an obstacle in space to smallness of size as to any given velocity of motion, and there are reasons for supposing that gravity must propagate itself with great velocity. Precisely because the normal velocity of the atoms is great, the material concerned in producing gravity can be very limited in quantity, and notwithstanding that exert a very considerable pressure. The atoms are therefore to be assumed very small, almost points, the condition adapted for a great length of path. The analogy of this gravitation mechanism (at least in principle) with the generally assumed structure of our atmosphere, may be regarded as a recommendation to the theory.

A further objection of Maxwell's, that according to this theory the action of gravity could only be kept up by an enormous expenditure of external work little short of ruinous, applies in fact to the theory of Le Sage in the form presented by Lord Kelvin; also to the theories of Isenkrahe and Bock considered further on; not, however, to the theory set forth by the present writer, because, according to this latter theory, the maintenance of the motion of the æther atoms demands just as little an expenditure of energy as the maintenance of the motion of the molecules of a gas in the ordinary gas theory. Moreover, the "shelter" of one mass by another is explained without any absorption of energy.

The large store of energy contained in the æther atoms is moreover of use for the explanation of the most varied natural phenomena; and it may be observed that the intervention of a medium is wanted in other respects, for instance for the elucidation of magnetic and electric phenomena.

It may be mentioned, further, that the explanation of gravitation carries with it the great advantage of rendering superfluous the idea of the existence of two (inherently different) kinds of matter, "ponderable" and "imponderable." The smaller atoms in space do not gravitate, only because the mechanism of gravitation cannot itself be subject to the conditions for producing gravitation. So, therefore, disappear the almost contradictory properties, "ponderable" and "imponderable," which have been arbitrarily attributed to matter: and we have therefore no reason for believing that the atoms diffused in space differ essentially from gross molecules, excepting in their dimensions. To the abandonment of the idea of two inherently different kinds of matter, the abandonment of two supposed different kinds of energy is analogous—viz., energy with motion, and energy without motion. Accordingly there would remain only one kind of energy, namely, that which a moving body possesses.

Another important quantitative relation is so conditioned that the "shelter" is evidently proportional to the surface exposed to the moving atoms; the gravitational effect, on the other hand, is proportional to the *mass*, as experiment shows. This result can only be achieved by supposing gross matter to possess a very porous structure. In that way, the gross molecules inside a body are reached or affected by the penetrating æther atoms almost with the same facility as the external molecules of the body. If we assume that the quantity of material contained in the substance of any molecule is very small compared with the vacant space contained in that same molecule, and if one does not suppose any superfluous material in the structure of the molecule; the proportionality existing between gravitation and *mass* can be satisfied as closely as observation requires.

Some Remarks on Crystal Structure.

Even Le Sage recognized that for the elucidation of the gravitational effects the assumption of a porous or open structure in matter is necessary. Lord Kelvin draws a curious inference from this. In the Philosophical Magazine, May 1873, postscript p. 331, Lord Kelvin supposes that it might be probable that bi-axial crystals would not be penetrable with equal facility in all directions by the æther atoms. If that were so, such crystals would possess a (even if very small) difference of weight, according as the one or the other axis is vertical. Have, however, sufficiently delicate experiments been made on this point?

A contribution published by me in the Philosophical Magazine for April 1880 on crystalline structure might be mentioned here.

I have tried to define further this open structure, so that it appears to be well adapted for the explanation of cohesion, adhesion, and chemical affinity.

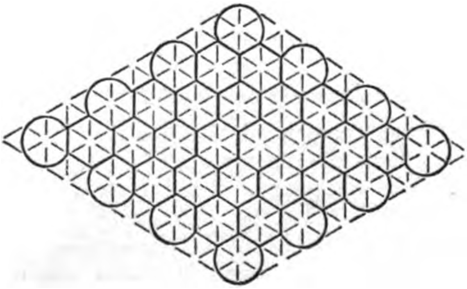
One knows how the cells of bees are formed by pressure, and how by pressure elastic spheres may be converted into angular, such as hexagonal-shaped, bodies.

As remarked, the gravitation theory (and many independent facts) demand that the molecules of bodies shall possess an open structure; which also satisfies the conditions of lightness and economy of material. As crystals exist, it is sometimes supposed that the molecules of bodies (whose open structure is often illustrated by cubes and other figures formed of wire) themselves represent the shapes of the crystals.

We do not, however, need to assume that the molecules possess exactly such shapes, because if the separate molecules themselves possessed even a rounded structure, they must be pressed into angular forms as soon as two or more of them were pressed together by impacts of the æther atoms. Let us take for illustration the simplest open structure, viz. rings; although it is not thereby implied that this is the sole ground-form of the molecules. Elastic molecules of any very open structure of three dimensions would probably give a greater stability to the crystal mass formed out of them.

Simple elastic rings can then by pressure of their boundaries against each other (as caused by the flying of very minute æther atoms through the structure) conceivably be changed into hexagonal, square figures, &c. Fig. 1 may serve to

Fig. 1.



show such a pressure-effect produced by atomic motion, where elastic rings are converted into the hexagonal forms of crystals. Cohesion (as now is generally supposed) is only gravitation * by contact. From the above considerations, it becomes easy to understand that elastic crystal forms can sometimes change into *non*-crystalline forms ; so some crystallizable metals, such as iron and zinc, lose all crystalline structure by rolling and hammering, and become ductile. Crystalline sulphur can, by mere warming, pass over into a sort of indiarubber sulphur. It is evident in fact that the irregular arrangement of the elastic molecules of a substance favours the gliding of the molecules over each other ; while, on the other hand, the regularly arranged molecules which are in contact at their boundaries (corresponding to crystalline structure) cannot be displaced at all without separating entirely : take for instance crystallized cast-iron and some other metals.

The freedom allowed to the molecules to arrange themselves in the case of solutions may be favourable for the production of crystalline structure, while rolling, hammering, &c., manifestly forces the molecules to aggregate in an irregular manner.

When elastic molecules of very open structure cross each other irregularly in all directions, or are arranged in parallel layers (as produced by the rolling of a metal), then it becomes obvious that a subsequent displacement of the molecules, as by a tensile-stress for example, does not necessarily produce actual severance ; but the atomic streams—from the very nature of this cause—can easily produce contact in fresh places, and so a gliding of molecules over each other is possible, without separation. So a bar of malleable iron gradually lengthens itself under a tensile-stress. On the other hand, because crystalline structure prevents all gliding of the molecules, it becomes impossible in this case for the atomic streams to cause contact in fresh places. The attempt to stretch a cast-iron bar, then, means separation of the molecules. I will not pursue these considerations more at length here : they may well be thought out into greater detail.

It may just be remarked, in passing, how elastic rings, fig. 2, can at first repel each other, merely on account of their elasticity of form ; and how in fig. 3, if the molecules are made to approach closer by force, this has as a consequence that the pressure of the atomic streams over the enlarged surface of contact overcomes the elasticity of form, and the

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* A fact observed by Prof. Dewar may be favourable to this view. The cohesion of metallic wires does not diminish (but rather the contrary) by a cold of −180° C. that of liquid oxygen. Now cooling of the metal could manifestly have no influence on the atomic streams, which are independent.

Fig. 2.

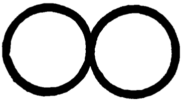
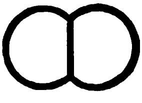


Fig. 3.



molecules cohere (which one calls "attraction"). As the converse of this, when the molecules are by a tensile-stress pulled nearly apart: then their elasticity of form can make the molecules suddenly spring apart of themselves, as, for instance, "unbreakable" glass flies into dust, when the molecular equilibrium is upset by a very sharp blow. Also, in general, if something is broken, the pieces will not readily unite of themselves, when placed in contact. The natural elasticity of shape of the elastic molecules causes an initial repulsion. By suitable assumption regarding thickness, stiffness, &c., of these ring-like molecular forms, the differences between the "chemical affinity" of different molecules might doubtless be accounted for.

Some may think that the above considerations are too simple to contain truth. Nevertheless one may rightly ask whether it is not precisely simplicity that one in general seeks in mechanism? The elucidation may serve as an initial explanation of certain obscure facts, which may develop itself further.

Respecting the elasticity of molecules (or atoms) Lord Kelvin makes the following observation:—

"We are forbidden by the modern physical theory of the conservation of energy to assume inelasticity, or anything short of perfect elasticity, in the ultimate molecules" (Phil. Mag. May 1873, p. 329).

The conception of elastic molecules (also illustrated in a striking manner by spectroscopic observations) appears, as said, to be a very practical conception for Physics, which is much needed. By this assumption the almost inconceivable idea of the sharp blows of "infinitely hard" molecules is avoided. On account of the perfect elasticity, all motions take place with "elegance" and smoothness, which permits a mobile equilibrium in nature, and (without due precautions) may well deceive the senses into the idea that in so-called "space" all is in repose.

It is a known consequence of the Newtonian law of gravitation, that the increase of attraction by diminution of distance is so small that two massive bodies, when they touch each other, attract each other so much the less the smaller they are; which one at once sees in the case of two spheres in contact, and can also demonstrate for bodies of other shapes. If, therefore, one attributes a massive structure to molecules, then, for the explanation of cohesion and chemical affinity. forces must be assumed which, by diminution of distance, increase quicker in intensity than according to the Newtonian gravitation law. On the other hand, the attraction of two cylinders of finite length and infinitely small section becomes infinitely great so soon as they touch each other. It is possible, therefore, on the basis of the here assumed open structure of matter, also to account for cohesion, adhesion, and chemical affinity, without necessarily having recourse to forces which, with diminished distance, augment quicker in intensity than the Newtonian law of gravity demands.

The Theory of Isenkrahe.

Two years after the present writer's first published paper, appeared the gravitation theory of Dr. Isenkrahe*, which attempts an explanation of gravity based on the kinetic theory of gases, and which seems in Germany to have become very well known. The author of this theory makes no mention of my theory, and it doubtless escaped his attention at that time.

The gravitation theory of Dr. Isenkrahe is founded on inelastic collision, which obviously involves the annihilation of energy, whereby the gas producing gravity would, after a certain (even very long) epoch, come to rest, and so gravitation cease to exist.

In a plausible enough way (at first sight at least) the author despises elasticity as a *qualitas occulta*, which, as he thinks, needs an explanation just as much as gravity itself. It seems, however, to have been overlooked that elasticity (at the encounters of molecules) is already demonstrated to exist by the principle of the conservation of energy, and of the centre of mass. The explanation of elasticity is a deeper one than the explanation of gravitation: therefore let us advance from step to step forward in the elucidation, without pushing on in too great a hurry.

All the consequences of the kinetic theory of gases are already built on the assumption of elasticity: the application of this principle to the smaller particles is therefore to be viewed as a perfectly natural and logical consequence. In fact the gravitation pressure by the encounters of elastic particles is *explained* quite as completely as the air-pressure is *explained* by the encounters of such particles (molecules). If one only accepts as valid the two principles of the conservation of energy and of the centre of mass, then one must attribute elasticity as well to the æther as to gas molecules, without being troubled about the further explanation of its nature.

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* *Das Räthsel von der Schwerkraft*, by Dr. C. Isenkrahe. (Vieweg & Sohn, Braunschweig, 1879.)

Therefore I have without hesitation regarded molecules of open structure as elastic, which implies that by the impact of such molecules no energy is annihilated. Dr. Isenkrahe regards the molecules of bodies as absolutely hard solid spheres which, in order that gravity by atomic encounters (*i. e.* its proportionality to *mass*) may be explained, must be far apart from each other. How can one imagine to oneself a structure composed of perfectly hard molecules situated far apart which shall have only tolerable stiffness and stability? Such a body made up of widely separated spherical molecules, if no other forces but gravity acted, could at the most behave like a gas, but never as a solid or liquid body.

On the other hand, elastic molecules of open structure may be made to cohere at their boundaries by the pressure of the smaller atoms, which at the same time easily fly through the open parts of the structure. Have we not here at least a groundwork for the conceptions upon which we may hope to build further?

Dr. Isenkrahe gives no limits for the value of the mean length of path, whereas it seems to me to be a very important point of my theory, that the mean length of path must be assumed great in comparison with the planetary distances.

Concerning the calculations which Dr. Isenkrahe attaches to his theory, Dr. A. M. Bock, who made the theory of Isenkrahe the basis of his 'Inaugural Dissertation'*, expresses himself as follows:—

"The aim and the purpose of the atomic æther theory, namely to construct universal gravitation, is, as mentioned in the introduction to the *Räthsel von der Schwerkraft*, not fully attained. There is no formula deduced from which, as a starting-point, one could follow out the theory further. One sees oneself forced therefore, in the sense of the theory, to deduce an (if only in some measure rigorous) expression for the attraction" (p. 18, under the paragraph-title *Die Anziehung zweier Körper*).

On the developments and modifications which Dr. Isenkrahe's calculations received through Dr. Bock I allow myself no opinion. The bases of them are nevertheless quite unaltered, and therefore open to the same objections; namely, he sets himself in contradiction with the principle of the conservation of energy, which, moreover, Dr. Bock himself admits.

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* Wolf & Sohn, Munich, 1891.

Hamburg, 1894.

APPENDIX (*added Jan.* 1895).—All who have thought on the subject know that, in the case of a falling body, the motion generated comes from the æther, according to any dynamical explanation of gravitation: and when the body strikes the earth's surface, shaking its molecules into vibration by the concussion, these ("heat") vibrations develop waves in the æther, or are "radiated" away. So we have a *cyclical* process here, where motion passes from a material agent and back again to that agent, in a circle.

In accordance with the above we see, then, that stars or stellar suns do not "pour their heat unrequited into space," but return their stores of motion to the source whence they were obtained. For if gravity be caused by a material agent, and if solar energy be derived from gravity, then manifestly solar energy is returning only to its original source, to be again available for generating heat (through gravitation) in some other regions of the universe.

Evidently, if chemical action be caused by a material medium, then an animal or a steam-engine lifting a weight is an instance (again) of motion coming from a material substance, and going back to it in a circle at the same time. A locomotive, as we know, converts all its energy into heat (which is radiated into the æther) as it progresses with its train: so clearly we have the cyclical process of exchange of motion again here: the same being true of work derived from falling water (cataracts) or from winds. If, finally, one pure speculation be permitted, we might suggest that overgrown stars may, towards their centres, become from excessive compression inadequately penetrable by the atoms of the æthereal gas, and so the overgrown masses be broken up by conversion of the æthereal motion into heat. Thus cyclical change would apply to the Universe generally: the stellar bodies constituting in sum a gigantic grained gas inside an excessively fine atomic one. For the tentative development of this idea, a paper in the Philosophical Magazine, August 1879, also *Sitzungsberichte*, April 1883, Vienna, may be mentioned. So it appears that the Universe may at present (in the same sense as a gas is) be in equilibrium of temperature.

XV. *Students' Simple Apparatus for Determining the Mechanical Equivalent of Heat.* *By* Prof. W. E. AYRTON *and* H. C. HAYCRAFT[*].

I. *The Object to be Attained.*

SOME time ago the authors considered the possibility of constructing an apparatus for the determination of the mechanical equivalent of heat which could be placed in the hands of junior students, and which would enable a sufficiently accurate result to be obtained without the introduction of troublesome corrections. For such a purpose the electrical method was naturally adopted; for now that the commercial values of the electrical units are known with considerable accuracy in the C.G.S. system, it is possible to measure energy in foot-pounds by means of a good commercial ammeter voltmeter and watch with greater ease and certainty than by any mechanical dynamometer.

Further, it has become easy to obtain as much electric power as is wanted for the experiment at a small cost, for the price of half a horse-power for ten minutes is only one-third of a penny, at 6*d.* per Board of Trade Unit. Hence there is not the practical objection to the electrical method that was so formidable when currents of 20 or 30 amperes could only be obtained by setting up a large battery of Grove or Bunsen cells. Indeed every properly organized physical laboratory is now provided with accumulators, from which a quarter or half a horse-power may be readily obtained for use in such experiments as those to be described; or, when accumulators are not available, power may be taken from the mains of one of the numerous electric-supply companies.

II. *Design of the Apparatus.*

The authors therefore set themselves to design an apparatus which, when used with a good commercial ammeter voltmeter, thermometer, and watch, would give the value of the mechanical equivalent of heat correct to one per cent. without any corrections having to be made even for the heat lost by radiation, convection, and conduction, and without any special manipulative skill being required on the part of the observer.

Broadly, the experiment consists in passing a known current through a resistance immersed in a known mass of water, and measuring the rise of temperature in a given time, and the average value of the P.D. between the terminals of the resistance.

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[*] Communicated by the Physical Society: read November 23, 1894.

It is evident that if the loss of heat during the experiment is to be small enough to be neglected in comparison with the quantity of heat generated, either the rise of temperature must be small, or must take place in a very short time, or the ratio of the cooling surface to the mass of the water heated must be small. As it is impracticable to reduce either the rise of temperature or the time to very small limits, and also to measure them with ease and accuracy, it is clear that the result is best obtained by using a large quantity of water, for the ratio of the surface area to the mass can then be made small enough to bring the error due to cooling within the required limits. But a large quantity of water necessarily involves the use of a large amount of electrical energy; and we thus arrive at the result that the accuracy attainable depends upon the amount of *power* at our disposal, and will be greater the greater the electric power that can be supplied.

In designing such an apparatus, then, the first thing to determine is the amount of electric power that can be used, and the details should then be arranged so as to get the least error in the result. In those cases in which an increased accuracy in one measurement involves a diminished accuracy in another, it is best to make the errors due to the two causes equal. For example, suppose that the time during which the electric energy is supplied is such that we can only measure it to one per cent., while the error due to cooling during the experiment is only ½ per cent. We can clearly increase the accuracy of the result if we increase the time until the probable error in reading it is equal to the error due to cooling during that time, say ¾ per cent. If we were still further to increase the time, the error due to cooling would increase and exceed ¾ per cent., and our result would therefore be less accurate. This equality of course does not apply to errors that are not interdependent, such as errors in reading volts and amperes: each of these errors should independently be be made as small as possible.

The measurements to be made are as follows:—

(*a*) The value of the constant current passed through the resistance.

(*b*) The average value of the P.D. between its terminals.

(*c*) The mass of water heated, to which must be added the water-equivalent of the containing vessel, resistance-coil, and stirrer.

(*d*) The rise of temperature of the water.

(*e*) The time during which the current is passed.

With the excellent electrical measuring-instruments now obtainable it is possible to measure either current or pressure with an accuracy much greater than one per cent.; indeed the Board of Trade undertake to measure them within one tenth part of one per cent.* We can also measure the mass of water with considerable accuracy : any error, even a large one, made in determining the water-equivalent of the other bodies raised in temperature becomes of small consequence when the water-equivalent is added to the much larger and accurately measured mass. The measurements (*a*), (*b*), and (*c*), therefore, give us little trouble and do not affect the design of the apparatus.

The case of (*d*) and (*e*) is different. In order to measure a change of temperature by means of a thermometer with the accuracy required, either the change must be fairly large or the thermometer must be very sensitive ; but as it is of little use to employ an exceedingly sensitive thermometer to measure the temperature of a liquid which is being locally and rapidly heated, even if the stirring is very efficient, it is necessary to use a fairly large rise of temperature. Similarly, if the circuit is to be closed and broken by hand, and the interval of time measured by an ordinary stop-watch such as would be found in a junior laboratory, there is a certain minimum time required to give the required accuracy of measurement. Also we must keep the ratio of heat lost to heat generated during the experiment equal to the probable error in the time or temperature-measurement; for as these three quantities are interdependent, the best condition is to make the percentage accuracy of the temperature measurement, the percentage accuracy of the time measurement, and the percentage heat lost of heat generated, equal.

Let W be the maximum number of watts at our disposal ;
M the mass of water, including water-equivalents ;
S the area of surface of the containing vessel ;
e the average emissivity of the cooling surface, or the ratio of heat lost in calories per second to the surface area, for 1° C. excess temperature ;
Θ the minimum change of temperature that can be measured to 1 per cent. under the prescribed conditions ;
T the minimum time, in seconds, between closing and opening the switch that can be measured by the stop-watch to 1 per cent. ;
θ the rise of temperature of the water ;
t the time during which the switch is closed ;

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* See Schedule to Final Report of Electrical Standards Committee, 1894.

and let $\frac{1}{x}$ per cent. be the maximum accuracy of result obtainable under these conditions.

Since $$\theta = x\Theta,$$

and $$t = x\mathrm{T},$$

and the ratio of heat lost to heat received is $\frac{1}{100x}$,

we have $$\frac{\mathrm{S} \,.\, x\frac{\Theta}{2} \,.\, \epsilon \,.\, x\mathrm{T}}{\mathrm{M} \,.\, x\Theta} = \frac{1}{100x},$$

or $$x^3 = \frac{2\mathrm{M}}{100\,\mathrm{S} \,.\, \epsilon \,.\, \mathrm{T}}. \quad . \quad . \quad . \quad (1)$$

We also know, say from preliminary experiments, that the heat received in calories is about 0·24 time the energy in watt-seconds.

$$\mathrm{M}x\Theta = 0{\cdot}24\,\mathrm{W}x\mathrm{T},$$

or $$\mathrm{M}\Theta = 0{\cdot}24\,\mathrm{WT}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In equations (1) and (2) M and x are the only unknown quantities, for S is a function of M depending on the shape of the vessel containing the water. Thus for a cylindrical vessel of height equal to its diameter,

$$\mathrm{S} = 5{\cdot}53\,\mathrm{M}^{\frac{2}{3}};$$

while for a spherical vessel,

$$\mathrm{S} = 4{\cdot}84\,\mathrm{M}^{\frac{2}{3}}.$$

We can therefore find both M and x from the equations, and since

$$\theta = x\Theta,$$

and $$t = x\mathrm{T},$$

θ and t are also determined.

It may be observed here that as S varies as $\mathrm{M}^{\frac{2}{3}}$, and x^3 varies as $\frac{\mathrm{M}}{\mathrm{S}}$, x is proportional to the 6th root of M or to the 6th root of W. Hence if the number of watts available is doubled the accuracy of the experiments is by no means doubled, but is only increased by about $\frac{1}{8}$th.

In the particular case for which the apparatus was designed the number of watts available was about 300, the maximum current being 30 amperes. This determined the resistance of the coil or strip as $\frac{1}{3}$ of an ohm.

The average emissivity for small excess temperatures of a glass vessel standing on a felt base and containing water was obtained by taking cooling curves, the mean value being 0·000232 calorie per square centimetre of area per 1° C. excess temperature. The water was kept at a uniform temperature by means of a light wooden stirrer during these experiments.

Θ, the minimum rise of temperature that can be measured to one per cent., was taken as 2·5 degrees, as it was not considered advisable to rely on the temperature measurements to more than $\frac{1}{40}$ of a degree. The thermometer used is read without the aid of a telescope, and is graduated in 20ths of a degree.

T, the minimum time that can be read to one per cent., was taken as a minute and a half, as it was thought that an error of nearly a second might be made in the measurement of the time between closing and opening the switch, and stop-watches are often a little doubtful as to their zero.

From equation (2) we have at once

$$M = \frac{0{\cdot}24 \times 300 \times 90}{2{\cdot}5}$$

$$= 2592 \text{ cubic centimetres.}$$

Substituting in equation (1), we have

$$x^2 = \frac{2}{100} \times \frac{\sqrt[3]{2592}}{5{\cdot}53} \times \frac{1}{{\cdot}00023} \times \frac{1}{90},$$

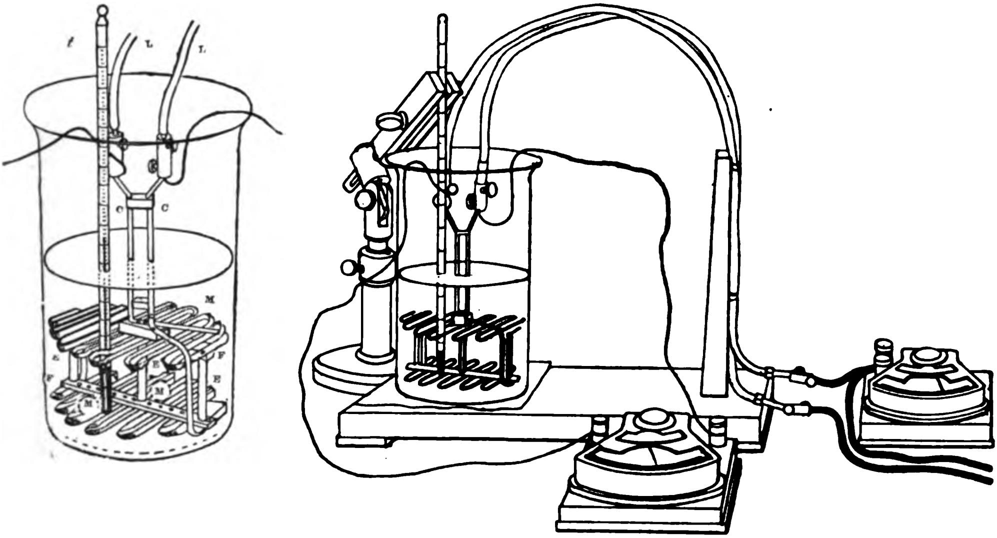
$$x = 1{\cdot}55\,;$$

or the accuracy of measurement is 0·64 of one per cent. The rise of temperature adopted should therefore be 3·87 degrees, the time being 2 minutes 20 seconds. The numbers actually adopted in the experiments were 2000 cubic centim. of water and a time of 2 minutes; the smaller quantity of water being adopted because the resistance of the immersed strip when made proved to be rather less than $\frac{1}{3}$ ohm, the watts taken at 30 amperes being 260 instead of 300.

To ensure success in an experiment of this kind it is necessary that the water be as uniformly heated as possible, and that the stirring be very efficient; and after some consideration the authors decided that the best of all plans would be to use a movable conductor of considerable surface, and so shaped that it might itself be used to stir the liquid. By this means an exceedingly uniform rise of temperature may be produced, every particle of water receiving heat direct from the strip at practically the same rate. The following is a description of the apparatus as constructed by the authors.

A strip of manganin (chosen on account of its low temperature-coefficient), about ¼ inch wide, 0·03 inch thick, and about 5 feet long, was bent into a series of zigzags (fig. 1) so as to

Fig. 1.



form a kind of circular gridiron, M M, in which the successive portions of strip lie all in one plane, the whole being held rigid by a strip of vulcanized fibre F crossing the gridiron and to which each portion of strip was screwed. Another precisely similar gridiron was placed 3 inches below the first, and they were held together by three thin ebonite pillars E screwed to the strips of vulcanized fibre, the whole forming the top and bottom of a sort of cylindrical box, 5 inches diameter and 3 inches high. The two grids were joined in series, and the ends of the strip of manganin were soldered to two copper wires C C, about 0·128 inch thick and 6 inches long, which were insulated from one another by vulcanized fibre separators, and constituted a kind of handle by means of which the open box could be moved up and down in the containing vessel.

The whole surface exposed to the water received a thin coat of varnish to prevent any electrolysis due to the difference of potential between the different parts of the strip. At two points in the same vertical line the zigzags forming the two grids are bent so as to leave a space for the passage of a thermometer *t*, the bulb of which is midway between the grids when the lower one is resting on the bottom of the vessel. The whole heating surface exposed to the water is about 60 square inches, or 400 square centimetres. The vessel used to hold the liquid is a thin glass beaker of just sufficient diameter to take the framework of manganin strip.

Electric connexion with the two stiff wires which form the handle is made by means of two well-insulated very flexible leads L L, each composed of a strand of about 210 copper wires ·011 inch diameter. The size of the stout copper wires and of the flexible lead was chosen with the intention that there should neither be heat received nor heat lost on account of these connexions. The sectional area of the insulated flexible lead is rather greater than that of the stout copper wires, and the ultimate rise of temperature of both with a current of 30 amperes is about 7° C.; the rise of temperature during the short time that the current is passed being thus about equal to that of the water, and automatically preventing gain or loss of heat. (The number of watts taken by the copper wires and flexible leads at 30 amperes is about 1·9.)

It may here be pointed out that it is far better, from the point of view of getting a good mechanical design, to use a large current at a low pressure than to take the same power from a small current at a considerable pressure. Thus it is easy to design a strong stirrer of the shape described above which will have a resistance of $\frac{1}{3}$ of an ohm, carrying 30 amperes at 10 volts pressure; but it would be by no means so easy to make an equally efficient and substantial stirrer of 33·3 ohms resistance to take 3 amperes only at 100 volts.

It was thought worth while to ascertain to what extent conduction through these leads influenced the rate of cooling of the vessel when no current was passing, and cooling curves were therefore taken with the manganin framework in the vessel and attached to the leads. The average rate of cooling was found to be 0·000242 calorie per square centimetre area of surface per 1° C. excess temperature; which is only about 4 per cent. greater than in the previously mentioned experiments, in which a light wooden stirrer only was used, the value then obtained being 0·000232.

III. *Use of the Apparatus.*

In the following table are given the results of several successive experiments made with the apparatus described above by Messrs. Solomon and Grogan, students at the Central Technical College, under our supervision. The amperes and volts are expressed in the international units adopted at the Chicago Congress. The ammeter and voltmeter used were the well-known Weston-d'Arsonval type instruments. The current was known within about $\frac{1}{5}$ of one per cent., and the average potential-difference within about $\frac{1}{5}$ of one per cent., the instruments having recently been tested against our standards at the Central Technical College. 2000 cub. centim. of water were used in all the experiments, and were measured with a graduated glass jar, fresh water being used in each experiment. The weight of the glass vessel up to the water-level was determined as 184 grammes, and the specific heat being about 0·2, the water-equivalent is 37 grammes. The weight of the manganin strip is 114 grammes, and the specific heat being about 0·09, the water-equivalent is 10; the equivalent mass of water used being therefore 2047 grammes.

No. of expt.	Time in seconds.	Temperature.			Amperes.	Mean volts.	Calories per watt-second.
		Initial.	Final.	Rise.			
1...	120	18·40	22·02	3·62	30	8·634	0·2383
2...	180	13·25	18·70	5·45	30	8·634	0·2390
3...	180	13·60	19·00	5·40	30	8·648	0·2367
4...	120	12·97	16·53	3·56	30	8·656	0·2375
5...	120	12·64	16·26	3·62	30	8·698	0·2365
6...	120	12·89	16·49	3·60	30	8·662	0·2364
7...	120	12·11	15·72	3·61	30	8·666	0·2368
8...	120	12·10	15·74	3·64	30	8·642	0·2395
9...	120	13·13	16·75	3·62	30	8·692	0·2367

Mean 0·2375

Average deviation from the mean = ·001 = 0·42 per cent.

With this apparatus, then, we get in about 10 minutes, including the experiment and subsequent calculation, a result for the heat-equivalent of the watt-second; and these results have an average deviation from the mean, if several experiments are made, of less than $\frac{1}{2}$ of one per cent. This result, as we have seen above, should not differ from the true value by as much as one per cent. It may here be pointed out that as the water taken from the ordinary water-supply is sure to be at least two or three degrees below the atmospheric temperature at the time, it is exceedingly easy to arrange that its mean temperature during the experiment shall be exactly equal to the temperature of the air, for no artificial method of cooling is required, as would be the case if a greater range of temperature were used. This, however, was not done except in one or two of the above experiments, and is not necessary to ensure the accuracy that was required.

The mean temperature of the water in the above experiments was 15 degrees Centigrade; and our final result is that at that temperature 0·2375 gramme of water are raised 1° C. in temperature by the energy of one watt-second.

Now we know with considerable accuracy the equivalent in ergs of one watt-second, which certainly does not differ from 10^7 by more than one tenth of one per cent.; that is to say, the international volt and ampere do not differ from 10^8 and 10^{-1} C.G.S. units of electromotive force and current by more than that amount (see section on the recent history of the electrical units). Hence the result we have obtained, the error in which is less than one per cent., gives us at once a value for the mechanical equivalent of heat with the same accuracy.

Since we find the equivalent of the watt-second in gramme-degrees at 15° C. to be 0·2375, we have at once, taking 10^7 ergs equal to one watt-second, the mechanical equivalent of heat in ergs per gramme-degree at 15° C. equals $\mathbf{4{\cdot}211 \times 10^7}$.

Reducing this to foot-lbs. at Greenwich per lb.-degree C. at 15° C., it becomes **1408**, or in foot-lbs. per lb.-degree F. at 59° F. it is **782**.

A series of four experiments made subsequently by some students at the Central Technical College, in which the cooling error was eliminated by making the mean temperature of the water equal to that of the air, gave as their mean 0·2384 calorie per watt-second, or $4{\cdot}195 \times 10^7$ ergs per gramme-degree at about ° C. Reducing this value to foot-lbs. at Greenwich per lb.-degrees C. and F. respectively, we get 1403 and 779 foot-lbs.

IV. *Previous Determinations of the Mechanical Equivalent of Heat.*

It is of interest to compare these figures with some of the more recent results obtained for the mechanical equivalent.

Rowland's value for the mechanical equivalent in ergs per gramme-degree at 15° C. is $4{\cdot}189 \times 10^7$, which reduced to foot-lbs. at Greenwich per lb.-degree C. is 1401, and in foot-lbs. per lb.-degree F. at 59° F. is 778·3. Rowland used the method of direct friction of water, and was the first to discover that the specific heat of water was a minimum at 30° C. and varied one per cent. between 5° and 30° C. (Proc. American Acad. 1879–80).

Dieterici (1889) gives as the result of a determination by the electrical method in which Bunsen's ice-calorimeter was used, the number $4{\cdot}244 \times 10^7$. Correcting from the "legal" ohm employed by him to the international unit, we get the numbers $4{\cdot}232 \times 10^7$, 1415, and 786 (*Annalen der Physik*, vol. xxxiii. p. 417).

Miculescu's careful determination by the direct method in

1892 gives $4{\cdot}186 \times 10^7$ on the mercury scale of hard glass, or 4·187 on the hydrogen scale, at about 12° C. The latter number expressed in foot-lbs. at Greenwich per lb. degree C. is 1400, and in foot-lbs. per lb. degree F. is 778. A platinum non-thermal junction was used in these experiments, and was calibrated against a Gonnelot standard mercury thermometer.

Griffiths, using the electrical method, gives as his final result (Proceedings Royal Society, vol. iv. p. 26), $4{\cdot}198 \times 10^7$, the corresponding numbers in the other units being 1404 and 780.

The recent determination of Schuster and Gannon, also by the electrical method, gives $4{\cdot}180 \times 10^7$ on the mercury scale of hard French glass, or 4·192 on the hydrogen scale, at a temperature of 19°·1 C. The latter value expressed in foot-lbs. at Greenwich gives 1402 and 779.

Joule's values obtained by friction of water in 1878 gave the numbers $4{\cdot}159 \times 10^7$, 1390·5, and 772·5 respectively (mercury scale); while his values obtained by the electrical method in 1867, when corrected for the error in the B.A. ohm, give $4{\cdot}155 \times 10^7$, 1389, and 772, the average temperature of the water being 19° C. The following table gives the results obtained by various methods since 1867, the numbers having been recalculated from those given in a table at the end of M. Miculescu's paper (*Ann. de Chimie*, vol. xxvii. p. 202) :—

Date.	Observer.	Method.	Ergs per gramme-degree C.	Foot-lbs per lb.-degree F.
1867.	Joule.	Electrical.	$4{\cdot}155 \times 10^7$	772
1870.	Violle.	Heating of a disk between the poles of a magnet.	$4{\cdot}269 \times 10^7$	793
1875.	Puluj.	Friction of metals.	$4{\cdot}179 \times 10^7$	776
1878.	Joule.	Friction of water.	$4{\cdot}159 \times 10^7$	772
1878.	Weber.	Electrical.	$4{\cdot}145 \times 10^7$	770
1879.	Rowland.	Friction of water 15°.	$4{\cdot}189 \times 10^7$	778
1888.	Perot.	By the relation $L = r(v_2 - v_1)\frac{dp}{dt}$.	$4{\cdot}167 \times 10^7$	774
1889.	Dieterici.	Electrical.	$4{\cdot}232 \times 10^7$	786
1891.	D'Arsonval	Heating of a cylinder in a magnetic field.	$4{\cdot}161 \times 10^7$	773
1892.	Miculescu.	Friction of water.	$4{\cdot}186 \times 10^7$	778
1893.	Griffiths.	Electrical.	$4{\cdot}198 \times 10^7$	780
1894.	Schuster and Gannon.	Electrical.	$4{\cdot}192 \times 10^7$	779

The results obtained since 1879 by stirring water and by electrical methods may be tabulated thus :—

Rowland (friction)	$4{\cdot}189 \times 10^7$ or 778,
Dieterici (electrical)	$4{\cdot}232 \times 10^7$ or 786,
Miculescu (friction)	$4{\cdot}186 \times 10^7$ or 778,
Griffiths (electrical)	$4{\cdot}198 \times 10^7$ or 780,
Schuster and Gannon. (electrical)	$4{\cdot}192 \times 10^7$ or 779.

The result obtained by our students is greater than the mean of these results by just one half per cent. It is probably not generally known that such accuracy can be obtained by the use of such simple apparatus as that here described, and the fact is we think sufficient justification for bringing the result under the notice of the Society.

V. *Recent History of the Practical Electrical Units.*

A short account of the recent history of the practical electrical units is added for the benefit of those not familiar with the work of the Board of Trade Standards Committee.

The first report of the Electrical Standards Committee, appointed by the Board of Trade at the end of 1890, was presented in July 1891, and contained the following recommendations among others :—

"4. That the resistance offered to an unvarying electric current by a column of mercury of a constant cross sectional area of one square millimetre and of a length of 106·3 centimetres, at the temperature of melting ice, may be adopted as one ohm."

"10. That an unvarying current, which when passed through a solution of nitrate of silver in water, in accordance with the specification attached to this Report, deposits silver at the rate of 0·001118 of a gramme per second, may be taken as a current of one ampere."

At the British Association meeting held at Edinburgh in August 1892 the B.A. Committee on Electrical Standards, in consultation with Dr. von Helmholtz, M. Guilleaume, Professor Carhart, and others, agreed to the following resolutions among others :—

"2. That 14·4521 grammes of mercury in the form of a column of uniform cross section 106·3 centimetres in length at 0° C. be the specified column of mercury adopted as the practical unit of resistance."

"That the number ·001118 should be adopted as the number of grammes of silver deposited per second from a neutral solution of nitrate of silver by a current of 1 ampere, and the value 1·434 as the electromotive force in volts of a Clark cell at 15° C."

These decisions agreed with those which had already been laid before the German Government by Dr. Helmholtz and the Curatorium of the Reichsanstalt. It was considered preferable to define the mercury column in terms of length and mass, as the sectional area cannot be directly measured with such accuracy; but the length 106·3 centimetres was adopted so that the sectional area might be, as nearly as could be known, one square millimetre, as this area has been specified in all previous definitions.

In November 1892 a supplementary report was presented to the Board of Trade by its Standards Committee, and included the following resolutions :—

"4. That the resistance offered to an unvarying electric current by a column of mercury at the temperature of melting ice 14·4521 grammes in mass of a constant cross sectional area, and of a length of 106·3 centimetres, may be adopted as one ohm."

"10. That an unvarying current which, when passed through a solution of nitrate of silver in water, in accordance with the specification attached to this Report, deposits silver at the rate of 0·001118 of a gramme per second, may be taken as a current of one ampere."

"14. That the electrical pressure at a temperature of 15° Centigrade between the poles or electrodes of the voltaic cell known as Clark's cell, prepared in accordance with the specification attached to this Report, may be taken as not differing from a pressure of 1·434 volts by more than one part in one thousand."

At the International Electrical Congress held in August 1893 at Chicago these values were adopted by the delegates as those to be recommended to their several governments as legal units.

The Board of Trade Committee, after having had laid before them the recommendation of the Electrical Congress, which was substantially that contained in their supplementary report of November 1892, presented their final report advising a legalization of the standards as defined, by an Order of Her Majesty in Council; and on August 23rd, 1894, this was effected, and the practical standards we may hope permanently settled.

Of the three units—ohm, ampere, and volt—the two former are defined on the C.G.S. system, and the latter as a secondary unit from the relation of the first two. The numbers given in the above-quoted resolutions as to the ohm and the ampere are the values which appear to represent most accurately the true volt and the true ampere. In the Report of the B.A. Standards Committee for 1892 is given a table showing the results of nine determinations of the ohm expressed in centimetres of mercury, made between 1882 and 1892; the mean of these results being 106·31, and the average deviation from this mean being ·015, or one part in 7000. We may therefore safely say that the ohm, as now defined, does not differ from 10^9 C.G.S. units of resistance by more than one part in two or three thousand.

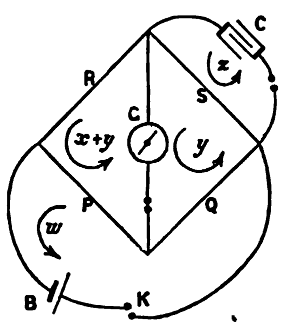
As regards the ampere, we have the very careful determination of Lord Rayleigh and Mrs. Sidgwick giving ·0011179 gramme of silver per coulomb, that of Kohlrausch ·0011183, Gray ·001118, and Potier and Pellat ·0011192. It is at least probable that the value ·001118 adopted by the Board of Trade Committee does not differ from that corresponding to the absolute C.G.S. unit divided by ten by more than one part in a thousand.

Hence it is probable that the number of ergs equivalent to one watt-second does not differ from 10^7 by more than one part in a thousand; and that being the case it would seem that, considering the great accuracy with which electrical measurements can be made, the electrical method of determining the mechanical equivalent of heat should be the most accurate.

XVI. *A Modification of the Ballistic-Galvanometer Method of Determining the Electromagnetic Capacity of a Condenser.*

By F. Womack*.

THE method consists in placing the condenser in parallel with one arm S of a Wheatstone-bridge arrangement of non-inductive resistances. A balance for steady currents having been obtained, the condenser is placed in circuit, and the throw θ determined due to the depression of the battery-key. The condenser is then thrown out of circuit, and the proportionality of the arms of the bridge disturbed by changing the value of S. The steady deflexion α due to this want of balance is read. From these two readings and the known values of S, the capacity is immediately determined.



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* Communicated by the Physical Society: read November 23, 1894.

If x, y, z, w denote the integral cyclic currents reckoned from the instant of make,

$$\left.\begin{array}{l} P(x+y-w)+\quad Gx \quad +R(x+y)=0 \\ \quad -Gx \quad +Q(y-w)+S(y-z)=0 \\ P(w-x-y)+\quad Bw \quad +Q(w-y)=\int E\,.\,dt \\ \qquad\qquad\qquad\qquad\qquad z=CS\dot{y}_\infty \end{array}\right\}$$

Substituting for z in the second equation and rearranging,

$$\left.\begin{array}{llll} (P+G+R)x+(P+R)y- & Pw & =0 \\ -Gx & +(Q+S)y- & Qw & =CS^2\dot{y}_\infty \\ -Px & -(P+Q)y+(P+Q+B)w & & =\int E\,.\,dt \end{array}\right\}\begin{array}{l}\text{(i.)}\\ \text{(ii.)}\\ \text{(iii.)}\end{array}$$

Hence

$$x=\frac{\begin{vmatrix} 0 & P+R & -P \\ CS^2\dot{y}_\infty & Q+S & -Q \\ \int E\,.dt & -(P+Q) & P+Q+B \end{vmatrix}}{\begin{vmatrix} P+G+R & P+R & -P \\ -G & Q+S & -Q \\ -P & -(P+Q) & P+Q+ \end{vmatrix}}=\frac{CS^2\dot{y}_\infty\begin{vmatrix} -(P+Q) & P+Q+B \\ P+R & -P \end{vmatrix}}{\Delta}$$

$$=\frac{CS^2\dot{y}_\infty}{\Delta}(PB+PR+QR+BR).$$

To find the steady current $\dot{y}_\infty$ ultimately flowing through S we have the same equations, except that the right-hand side of (ii.) is zero, and $\dot{x}_\infty$, $\dot{y}_\infty$, $\dot{w}_\infty$ instead of x, y, w. Hence

$$\dot{y}_\infty=\frac{\begin{vmatrix} P+G+R & 0 & -P \\ -G & 0 & -Q \\ -P & E & P+Q+B \end{vmatrix}}{\Delta}=\frac{E}{\Delta}(PQ+GQ+RQ+PG).$$

Therefore the integral current through the galvanometer is

$$x=\frac{CS^2E}{\Delta^2}(PB+PR+QR+BR)(PQ+GQ+RQ+PG).$$

When the balance is disturbed by S becoming S+dS, the cyclic equations for steady currents are

$$\left.\begin{array}{llll} (P+G+R)\dot{x}_\infty+ & (P+R)\dot{y}_\infty & -\quad P\dot{w}_\infty & =0 \\ -G\dot{x}_\infty & +(Q+S+dS)\dot{y}_\infty- & Q\dot{w}_\infty & =0 \\ -P\dot{x}_\infty & -\quad (P+Q)\dot{y}_\infty & +(P+Q+B)\dot{w}_\infty & =E \end{array}\right\},$$

which give

$$\dot{x}_{\infty}=\frac{\begin{vmatrix}0 & P+R & -P\\ 0 & Q+S+dS & -Q\\ E & -(P+Q) & P+Q+B\end{vmatrix}}{\Delta \text{ nearly}}=\frac{EP}{\Delta \text{ nearly}}dS,$$

assuming the value of the determinant Δ to be but little affected by the change of S.

Therefore, finally,

$$\frac{x}{\dot{x}_0}=\frac{T}{2\pi}\cdot\frac{2\sin\theta/2}{\tan\alpha}\times\text{correction for damping}$$

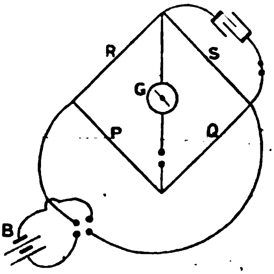
$$=\frac{CS^2}{\Delta}\cdot\frac{(PB+PR+QR+BR)(PQ+GQ+RQ+PG)}{P\,.\,dS},$$

which on expansion of Δ gives $\frac{CS^2}{dS}$;

$$\therefore\quad C=\frac{T}{2\pi}\cdot\frac{2\sin\theta/2}{\tan\alpha}\cdot\frac{dS}{S^2}\times\text{correction for damping.}$$

In the practice of the method, in order to avoid error arising from the altered value of Δ due to the change of S, readings of the deflexion, α may be taken with equal positive and negative values of dS. Thus an error which otherwise might be as great as 1 in 100 is reduced to 1 in 10^4.

In order to avoid change of the E.M.F of the battery due to its being for any appreciable time on open circuit, it is desirable to use a reversing-key in the battery branch, and to observe the throw of the galvanometer due to reversal of the sign of the current in S; and immediately after observe the deflexion due to the alteration of S.



The method is necessarily subject to the same disadvantages as that of Fleeming Jenkin, in respect of it not giving the instantaneous capacity of the condenser. But measurements of the same condenser taken with different galvanometers, or with a graded moment of inertia of the galvanometer-needle, have led to nearly constant results, the capacity being apparently but little dependent on the period of charging and discharging of the condenser. The effect would be likely to be much more marked if the capacity were much greater.

The conditions for a maximum throw of the galvanometer for a given E.M.F. are, moreover, not the same as those for the maximum sensitiveness to steady current. There is usually no difficulty, however, in obtaining sufficient sensitiveness of galvanometer to detect want of proportionality of the arms P Q R S of the bridge, so that a change of S by 1 in 200 will thus give a deflexion of convenient magnitude. It is, however, very advantageous to have a galvanometer whose period of oscillation can be varied at pleasure, so as to give about the same throw as steady deflexion for the chosen value of dS. One advantage which the method has is that there is no necessity to know the galvanometer or battery resistance. In the ordinary ballistic-galvanometer method it is very doubtful if the resistance of the galvanometer, unless it is measured at the time, is known within 1 to 2 per cent.

Further, the two essential parts of the determination θ and α may be made in quick succession, without any shifting of contacts or connexions and with the battery-current flowing continuously, leaving only the period of the galvanometer and its damping correction to be afterwards determined.

The method may be of service in the simultaneous determination of the resistance of, and joint capacity and inductance of, a submarine cable or telephone- or telegraph-line.

XVII. *Electrical Notes.* *By* Arthur Schuster, *F.R.S.*[*]

II. *On the Measurement of Resistance.*

A NUMBER of physical instruments, like the bolometer and platinum thermometer, depend on an accurate measurement of electric resistance. The question not unfrequently therefore arises, what the limit of accuracy is with which, with a given galvanometer and resistance, the measurement can be made.

Whatever arrangement we adopt, the sensitiveness is always increased by an increase of electromotive force; and the limit is reached either when we have put into action all the electromotive force at our disposal, or when the currents become so strong that there is danger of overheating one or other of the resistances. The overheating may either damage the insulation or produce disturbances in the way of thermo-electric currents, or be the cause of other irregularities. For a given resistance, we may generally fix on some current which is the greatest that can with safety be used. In ordinary laboratory practice our battery-power is generally sufficient, so that it is the heating of the conductors which puts the limit to a measurement of resistance; and I propose to discuss the question from this point of view. It may be answered in a very simple manner. Imagine any network of conductors, and let i be the current which passes through the resistance to be measured (p). Consider a small change of resistance δp. This change will alter the currents, and, amongst others, that passing through the galvanometer which forms the measuring instrument. The change in the currents is the same as if an electromotive force numerically equal to $i\delta p$ was introduced into the branch of which p forms part. In order that this electromotive force should affect the galvanometer, which we take to have a resistance g, there must be some one mesh of the network of conductors which contains both p and g. If there should be no other resistances in that mesh, and if p does not form part of any other mesh, the current $\delta\gamma$ in the galvanometer produced by the change of resistance δp will be given by

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[*] Communicated by the Author.

$$\delta\gamma=\frac{i\delta p}{p+g}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If the above conditions are not satisfied, and they never can be completely, the current through the galvanometer will be smaller than the value given. It will be shown that we may make such experimental arrangements as will render equation (1) approximately correct; at any rate, that equation will give us a lower limit for the change of resistance δp which produces an appreciable effect, if for i we substitute the maximum current which can pass the resistance. If this is denoted by i_m, and if $\delta\gamma$ stands for the smallest current the galvanometer can detect, we obtain

$$\frac{\delta p}{p+g}=\frac{\delta\gamma}{i_m}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This represents a somewhat important proposition:—

With a given resistance and galvanometer, the ratio of the smallest change of resistance which can be detected to the sum of the given and galvanometer resistance is equal to the ratio of the smallest current which can be detected by the galvanometer to the maximum current which can be sent through the resistances.

If we have a choice of galvanometers and take account of the fact that for the same type of instrument the deflexion varies as the square root of the resistance, equation (2) shows that the best galvanometer-resistance is that for which $p=g$, and in that case

$$\frac{\delta p}{p}=\frac{2\delta\gamma}{i_m}. \qquad \qquad (3)$$

With a given conductor and type of galvanometer, the smallest change per unit-resistance which can be measured is given by twice the ratio of the smallest current which can be detected by means of a galvanometer having the same resistance as the one to be measured to the greatest current which can be sent through the galvanometer.

For the smallest current which can be observed with a galvanometer of given type we may write $\delta\gamma=\alpha/(\sqrt{g})$. Inserting this in equation (3) and observing that the equation holds only when $p=g$, we obtain

$$\frac{\delta p}{p}=\frac{2\alpha}{\sqrt{i^2{}_m p}}; \qquad \qquad (4)$$

or:—

The highest percentage accuracy with which a given resistance can be measured is directly proportional to the square root of the maximum electric work which can be done on it without overheating.

Sometimes the galvanometer-resistance is given but p may be varied, as when we wish to design a bolometer or platinum thermometer. Equation (2) shows that there will be an advantage in taking p as large as possible provided we do not thereby reduce the value of i_m. This can be done by increasing the length of the conductor without diminishing the cross section.

The case which most frequently occurs is the one in which we have a certain, but not unlimited, choice of galvanometer. Each laboratory will probably be provided with a low and a high resistance galvanometer; but we cannot for each individual measurement construct one which has exactly the right resistance. It is useful to realize, therefore, how much we lose in sensitiveness by working with a galvanometer which has not exactly the right resistance.

Substituting again $\alpha/(\sqrt{g})$ for $\delta\gamma$, the smallest observable change of resistance δp then becomes

$$\delta p=\frac{(p+g)}{\sqrt{g}}\frac{\alpha}{i_m}.$$

If we further put $g = np$, where p is equal to the best galvanometer-resistance,

$$\delta p = \sqrt{p} \cdot \frac{n+1}{\sqrt{n}} \cdot \frac{a}{i_m}.$$

With a galvanometer of resistance np the sensitiveness is therefore $\frac{2\sqrt{n}}{n+1}$ times that of the obtainable maximum. And the reduction is the same whether the galvanometer-resistance is np or p/n. The following table giving the values of $\frac{2\sqrt{n}}{n+1}$ may be useful.

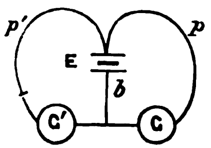
n.	$\frac{2\sqrt{n}}{n+1}$.	n.	$\frac{2\sqrt{n}}{n+1}$.
1	1	11	·553
2	·943	12	·533
3	·866	13	·515
4	·800	14	·499
5	·745	15	·484
6	·700	16	·471
7	·661	17	·458
8	·629	18	·447
9	·600	19	·436
10	·575	20	·426

It is seen that if the galvanometer-resistance is five times too great or too small, the sensitiveness is reduced by 25 per cent. Except for very special purposes, such a reduction is not of great importance; but I think sufficient consideration is not paid, in ordinary laboratory practice, to the proper choice of galvanometer-resistance. The tendency is to use a galvanometer of too great resistance, probably because the makers take more trouble with the more expensive instruments, and in consequence they are more easily adjusted and less liable to get out of order. With the same instrument it is convenient to be able to vary the resistance; and this can be done by using the pattern of a differential galvanometer, and by dividing each of the two coils again into two parts. The resistance may be varied in that case in the ratio of 1 to 16. If we had the command of three galvanometers each having four coils respectively of ·01, 4, and 1000 ohms, we could measure resistances varying between ·0005 and 20,000 ohms, and always be within 25 per cent. of the greatest obtainable sensitiveness so far as the galvanometer is concerned. If we are only able to have one galvanometer, we can obtain a useful combination by choosing one of four coils of about

10 ohms resistance each. By joining them in multiple arc or series, we may change the internal resistance from 2·5 to 40 ohms, and conduct measurements of resistances lying between half an ohm and 200 ohms with considerable accuracy.

We have obtained a value for the smallest change of resistance which it is possible to measure with any arrangement, but have not discussed how closely we may approximate to the theoretical value by any of the known methods. The simplest arrangement, in many ways, is that in which a differential galvanometer is used, as in fig. 1. The two nearly equal resistances to be compared are p and p', while G and G$'$ denote the two coils of the galvanometer. If balance is obtained with a current i_m passing through the resistances, it is required to determine the change δp which will produce the smallest observable change of current $\delta\gamma$ in the galvanometer. Equation (1) will be applicable if the internal resistance of the battery b is small compared to $p+g$; for in that case a small change of resistance δp will not disturb appreciably the current in G$'$, and will produce the maximum effect in its own branch.

Fig. 1.



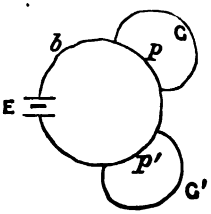
In order that this arrangement shall be workable, it is necessary, however, that the maximum current i_m which can pass p shall also be able to pass through the galvanometer without overheating it. Calling γ_m the greatest current which the instrument will stand, we have as a necessary condition that $\gamma_m \geqq i_m$.

As a second case, we take a differential galvanometer, but place it in parallel circuit with the resistance p. The arrangement is diagrammatically represented in fig. 2.

In order that an electromotive force $i\delta p$ shall produce a current $\frac{i\delta p}{p+g}$ in the galvanometer-branch G, it is necessary that b should be large compared with the combined resistance of p and g. The current through the galvanometer will be $\frac{ip}{g}$; and hence with this arrangement it is necessary that

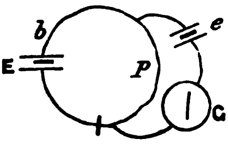
$$\gamma_m \geqq i_m p/g.$$

Fig. 2.



We might substitute an ordinary galvanometer for the differential one, but balance the current by an independent battery, as we frequently do in the comparison of electromotive force. The arrangement is that shown in fig. 3. A small change δp of p will show itself as a deflexion of the galvanometer. The sensitiveness is the same as before, with the exception that the resistance q of the auxiliary battery is a disadvantage. If b is large, we now have

Fig. 3.



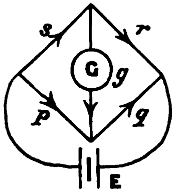
$$\frac{\delta p}{p+q+g}=\frac{\delta\gamma}{i_m}.$$

If we can make q small, we come back to the original equation; and I have introduced this example merely to show that however much we may vary the form of the experiment, we always come back to the same limiting value.

The method most usually adopted for a comparison of resistances is the Wheatstone-bridge, which is generally assumed without further discussion to be the most delicate arrangement.

It seems advisable, therefore, to discuss a little more fully the conditions under which the best effects can be obtained. If p is the resistance to be measured, we see at once that if a change of resistance δp produce a current $i\delta p/(p+g)$ in the galvanometer-branch, the resistance s must be small and q large compared to p and g. The arrangement is therefore very different from that we are usually told to adopt. To determine the effect of a small electromotive force $i_1\delta p$ in the branch p, let i_1, i_2, i_3, i_4, γ be the currents in p, q, r, s, and g respectively; then, in the usual way, we find in terms of the current in p,

Fig. 4.



$$\gamma=\frac{(pr-qs)i_1}{g(s+r)+s(q+r)}.$$

When the resistance p after being balanced is changed to δp, the current through the galvanometer will be

$$\delta\gamma=\frac{ri_1\delta p}{g(s+r)+s(q+r)}=\frac{ri_1\delta p}{g(s+r)+r(p+s)}. \quad . \quad . \quad (5)$$

In order that $\delta\gamma$ should be as great as possible, s must be as small as possible. If it can be neglected compared with p, we should have

$$\delta\gamma=\frac{ri_1\delta p}{g(s+r)+rp}.$$

If, further, q is large compared with p, and therefore r large compared with s, we obtain the fundamental equation,

$$\delta\gamma = \frac{i_1\delta p}{p+g}.$$

If all resistances are equal, which is often supposed to be the most favourable arrangement, the smallest detectable change of resistance δp is given by

$$\frac{\delta p}{p} = \frac{4\delta\gamma}{i_m};$$

that is to say, we only obtain half the maximum sensibility.

In the general case the best galvanometer-resistance is found to be

$$g = \frac{r(p+s)}{(r+s)};$$

and by introducing this value into equation (4), we obtain

$$\delta p = 2(p+s)\frac{\delta\gamma}{i_m}.$$

Also

$$\delta\gamma = \frac{\alpha}{\sqrt{g}} = \frac{\alpha\sqrt{r+s}}{\sqrt{r}\sqrt{p+s}}.$$

Hence

$$\frac{\delta p}{p} = 2\alpha\sqrt{\left(1+\frac{p}{q}\right)\left(1+\frac{s}{p}\right)}\frac{\delta\gamma}{i_m}.$$

This equation shows what we lose in sensitiveness by making s too large or q too small. If Carey Foster's method is adopted, $p=q$, and the sensitiveness is necessarily reduced in the ratio of $\sqrt{2}:1$.

The results here obtained are valid so long as we have sufficient battery-power at our command. If we are limited to a fixed and insufficient electromotive force, the conditions are altogether different, and in that case the problem has been fully discussed by Mr. O. Heaviside (Phil. Mag. 1873, xlv. p. 114).

M. Ch. Eug. Guye*, in a valuable paper, has discussed the best arrangement of a Wheatstone-bridge for bolometer measurements, but he only considered the special case of the equality between two and two of the four resistances. His results are in agreement with those given above.

In comparing the different methods of measuring resistance, we see that there is really no theoretical advantage of the Wheatstone-bridge over any other balance method. We obtain for all of them, on the contrary, the same limiting value. When a differential galvanometer is used, the two opposing currents pass through the coils of the instrument. Whenever there is any danger of disturbances in the indications of the needle due to heating-effects within the galvanometer, the Wheatstone-bridge will have the advantage. I do not know whether there are any actual measurements as to the strongest currents we can send through a mirror-galvanometer; but it seems likely that when the resistances to be measured are such that weak currents only can be used, as with a platinum thermometer or bolometer, the differential arrangement will possess many advantages.

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* *Archives des Sciences physiques et naturelles*, January 1892.

It appears that, in order to obtain the best effects from a Wheatstone-bridge, the resistance to be measured must adjoin one which is small and one which is great compared to itself; and these resistances must of course be constructed so that they are not overheated when the maximum current passes through the resistance which is to be measured. This we may not be able always to accomplish easily, and in practice the sensibility of the Wheatstone-bridge may have to be reduced still further. I think, therefore, that for measurements of resistance in which a high degree of accuracy is required, the differential galvanometer deserves more attention than it has so far received. If galvanometers can be constructed so that convection-currents due to heat-effects in the cell containing the suspended magnets can be avoided, it is very probable that the differential galvanometer will often prove to be the most suitable instrument.

With respect to the maximum current which we may be capable of sending through galvanometers of the same type, it is to be noted that the magnetic field at the centre of the coils is proportional to the square root of the electric work done in the instrument. When the heating-effect has reached the maximum allowable limit, the magnetic fields in different instruments having similar coils, but wound with different wires, will be the same.

The proposition embodied in equation (4) may give some useful hints in the construction of bolometers or platinum thermometers. Thus we may ask the question whether for certain purposes some other metal may with advantage be substituted for platinum.

The rise in temperature of a conductor δt is connected with the electric work (W) by the equation

$$Ms\delta t = W,$$

where s is the heat-capacity in electric units (water $=4{\cdot}49$). For a certain allowable gain in temperature per unit time and a given mass, that material is the best which has the greatest specific heat. A metal of low atomic weight would therefore have the preference. If the volume of the substance be taken as fixed, we must make the product of density and specific heat as great as possible. This product is highest for iron and steel (·90), then follows copper (·80), platinum (·72), and gold (·62). There would be an appreciable advantage in substituting a steel wire for a platinum one, if small differences of temperature are to be detected by a change of resistance, especially as the temperature-coefficient of electric conductivity is considerably higher than that of the other metals. There are, however, obvious disadvantages connected with the use of steel which in most cases would counterbalance its greater sensibility.

XVIII. Ronayne's *Cubes*.

By Professor H. HENNESSY, *F.R.S.*[*]

A FEW years since I was presented by Mr. S. Yeates with a pair of equal cubes, one of which could pass obliquely through the other. These objects had been for a long time in his father's possession, but there was no record as to where or by whom they were made. At first I paid little attention to the cubes, as I looked upon them merely as mathematical curiosities. Not long since, on perusing Gibson's 'History of Cork,' I came on a passage extracted from Smith's 'History of Cork,' published in 1750, in which a pair of interpenetrating cubes is distinctly referred to as the invention of Mr. Phillip Ronayne, of the Great Island near Cove (now Queenstown). The cubes were said to be constructed after Mr. Ronayne's design by Mr. Daniel Voster, who was at this time teacher of mathematics in Cork, and editor of the well-known book on Arithmetic, compiled during the early part of the last century by his father, Elias Voster[†].

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[*] Communicated by the Author.

[†] Passage in Smith's 'History of Cork':—

"Not far from the castle of Belvelly is Ronayne's Grove formerly called Hodnets Wood; [now Marino] a good house and handsome improvements of Philip Ronayne, Esquire. From the gardens one has a charming view of the river and shipping up to Cork, as also the town of Passage on the opposite shore. This gentleman has distinguished himself by several essays in the most sublime parts of mathematics; among others by a treatise on Algebra, which has passed through several editions, and is much read and esteemed by all the philomaths of the present time. He has invented a cube which is perforated in such a manner

I was led by this passage in Smith's 'History' to more closely examine the cubes, together with the box in which they are contained. The box is mahogany, and it is fastened by hasps of an old-fashioned pattern; it is itself manifestly in an old style of work. One of the cubes is made of hard wood, the other consists of a brass shell or frame, in which two pieces of hard wood fill up the vacant space so as to constitute a complete cube. The brass work was not a casting, but the result of combining pieces of hammered or sheet-brass suitably cut out which were welded or soldered together, and the whole was manifestly finished by the use of file and hammer. The only mark on the brass is the number 1, placed on a part of the shell as a guide for inserting one of the supplementary wooden pieces. This figure is undoubtedly in the old style, and Mr. Yeates is distinctly of opinion that the brass work is old-fashioned, as he satisfied himself, by comparing it with old brass instruments, that it could be very well assigned a date in the early part of the eighteenth century. It was most probably the work of an amateur, or done under the direction of a mathematician for a special object; for if it had been made by an instrument-maker for the purpose of sale a number of similar brass cubical shells could more easily have been made by casting.

I have never seen any demonstration of the structure of the cubical shell, but it soon appeared manifest that it is based on the properties of a square. Lay off on the diagonal of one of the faces of the cube from its middle point two parts, each equal to half the side of the cube. Draw lines at the extremities of these perpendicular to the diagonal, and two isosceles right-angled triangles will be formed which constitute the bases of two equal triangular prisms, between which a cube equal to that from which the prisms were cut can slide. If the cube slides parallel to the faces of the original cube the prisms will be totally unconnected, and the whole problem turns upon their material connexion while allowing the sliding cube to pass between them.

The annexed figures show the cubes separately, and also

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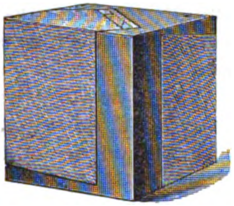
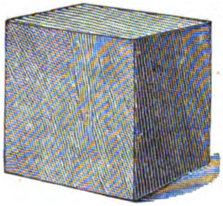
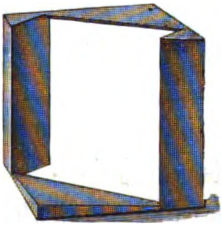
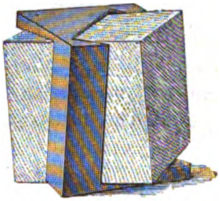
that a second cube of the same dimensions may be passed through the same, the possibility of which he has demonstrated, both geometrically and algebraically, and which has been actually put in practice by the ingenious Mr. Daniel Voster of Cork, with whom I saw two such cubes." (Smith's 'History of Cork,' 1st edition, 1750, vol. i. p. 172.) This passage is quoted by Gibson, who says that Daniel Voster was probably father to Elias, the author of the Arithmetic. But this is not correct—Daniel was the son of Elias, as I find from the eighth edition published in 1766 that Daniel was editor of the book to which the name of Elias is prefixed as the author.

the penetration of the second cube through the brass which forms the frame of the first.









The prisms must be connected at top and bottom by two similar and equal flanges, the edges of which must lie between the diagonal of the cube and the extreme corner of the flange. If too far from the diagonal, connexion with the prisms would cease; if too close to the diagonal, the second cube could not pass between the flanges.

The geometrical conception of a cube and the material solid representing such a conception to the sight and touch are different things. It is easy to conceive how one geometrical cube can pass through another of equal dimension by a square opening whose diagonals are perpendicular to the sides of the first cube. The triangular prisms left by this opening would be equal; but they would touch by mere lines, and could not be represented by a continuous solid material substance. They would necessarily be distinct and separate.

If the second cube were passed through the first parallel to the diagonal of the square on one of its faces, two triangular prisms would be cut off each distant from the other by the side of the cube. The sides of the base of each prism p would be manifestly $p=a\left(1-\frac{1}{\sqrt{2}}\right)$, and the long sides $a(\sqrt{2}-1)$. But these prisms would again be unconnected. They could be connected by triangular flanges having knife-edges, and equally inclined planes terminating at the corners of the cube. These knife-edges must manifestly be equal to the side of the cube; and as the sliding cube on each flange has its side perpendicular to the flange, the two flanges must have their edges a little distant from the diagonal to which each is parallel. The interval secures junctions of the flange with the two prisms. The thickness t of flange downwards must be also secured in order that the flange holds its place. The inclination of the face of the flange will depend upon these two quantities.

The relations between x the distance of the knife-edge from the corner of the cube, t the thickness of the flange at the points of junction with the prisms, and θ the angle of inclination of the inner face of the flange to the face of the cube can be easily found. As the sliding cube must have one of its sides always perpendicular to the face of the flange, the following equation must subsist:—

$$a=(a-t)\cos\theta+[p\sqrt{2}-(x-\tfrac{1}{2}a)]\sin\theta.$$

As the least thickness of the flange parallel to the long side of the prism may be represented by

$$t=(x-\tfrac{1}{2}a)\tan\theta,$$

the above becomes

$$(a-2t)\cos\theta+p\sqrt{2}\sin\theta=a, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or

$$a=a\cos\theta+[p\sqrt{2}-2(x-\tfrac{1}{2}a)]\sin\theta,$$

$$a-a\cos\theta=a(\sqrt{2}-2x)\sin\theta, \quad . \quad . \quad . \quad (2)$$

remembering that $p=a\left(1-\frac{1}{\sqrt{2}}\right)$.

From (2) the relation between x and θ gives for θ,

$$\sin\theta=\frac{2a(a\sqrt{2}-2x)}{3a^2+4x^2-4ax\sqrt{2}}.$$

From (1) the value of θ which makes t a maximum can be found by the usual methods,

$$2t=a(\sqrt{2}-1)\tan\theta-a(\sec\theta-1),$$

$$2\frac{dt}{d\theta}=\frac{a(\sqrt{2}-1)}{\cos^2\theta}-\frac{a\sin\theta}{\cos^2\theta},$$

$$2\frac{d^2t}{d\theta^2}=\frac{a\cos^3\theta-2(\sqrt{2}-1)\cos\theta\sin\theta-2a\sin^2\theta\cos\theta}{\cos^4\theta}.$$

When $\frac{dt}{d\theta}=0$, $\sin\theta=\sqrt{2}-1$, this, substituted in the value for $\frac{dt^2}{d\theta^2}$, shows that the latter must be negative; hence $\sin\theta=\sqrt{2}-1$ gives for t a maximum, or $\theta=24^\circ\,28'$ would give the greatest thickness for t. Between this and zero the thickness would give a smaller inclination and also a different value for x. In the model x has been chosen between the two extreme values $\frac{a}{\sqrt{2}}$ and $\frac{a}{2}$, or $x=\frac{a}{4}(\sqrt{2}+1)$.

This value of x would allow greater values of t and θ than in the model, but they have been both determined by making the greatest thickness of the flange at its extreme end equal to $\frac{p}{2\sqrt{2}}$. This gives

$$\tan\theta=\frac{p}{2x\sqrt{2}}$$

$$=\frac{p\sqrt{2}}{4x};$$

with the assumed value of x,

$$\tan\theta=\frac{\sqrt{2}-1}{\sqrt{2}+1}.$$

Hence $\theta=9^\circ\,45'$ nearly.

The value of x numerically is $a\,.\cdot60355$ nearly.

$$p=a\,.\,29289,\quad t=\frac{a(\sqrt{2}-1)^2}{4(\sqrt{2}+1)}=\frac{a}{4}\,\frac{(3-2\sqrt{2})}{(1+\sqrt{2})},$$

$$t=\frac{p^2}{8x}.$$

The side of the cube is very nearly 1·92 inch, and the above results agree with the measured values of x, p, θ, and very nearly with that of t.

It thus follows that a material solid cube can be so constructed as to allow of a cube of the same dimensions passing through it by an aperture cut in the former without separating the remaining portions. As crystals are known to be penetrated by others of similar shape, this problem may possibly illustrate questions connected with the study of isomorphous groups of the cubical type which are frequently known to present the appearance of interpenetration.

XIX. *On the Liquefaction of Gases.*
By Prof. Dr. CHARLES OLSZEWSKI[*].

MY researches concerning the liquefaction of gases, with which I have been occupied ever since the year 1883, have been published in various scientific periodicals in the Polish, French, and German languages, viz., in the publications of the Academy of Sciences of Cracow (in Polish), in the *Bulletin International* of the same Academy (in French and German), in the *Annals* of the Academy of Sciences of Vienna, and in Wiedemann's *Annalen der Physik und Chemie* and in his *Beiblätter*, as well as in the *Comptes Rendus.* Though I suppose that my labours are sufficiently known to the scientific world, yet there are motives which lead me to ask the Editors of the Philosophical Magazine to insert the following summary of the more important results of my experiments.

Firstly, because my researches appeared irregularly in different scientific papers, as they proceeded; such as wished to become acquainted with them being obliged to look them up in all the papers I have mentioned. Secondly, because of the experiments and public lectures of Prof. James Dewar, concerning the liquefaction of large quantities of oxygen and air. In several cases Prof. Dewar merely repeated my experiments: for instance, as regards the absorption spectrum and the colour of liquefied oxygen. In these cases he confirmed the observations I have made, and mentioned the results of my work in the manner usually received in the scientific world. But in his last experiments and lectures respecting the liquefaction of considerable quantities of oxygen and air and their employment as cooling agents, Prof. Dewar has thought fit not to make any mention of my labours in the same field, which had been published several years before Prof. Dewar went over them again. In the number for June 1890 of the *Bulletin International de l'Académie de Cracovie*, I have described an apparatus serving to liquefy a greater quantity of oxygen or air in a steel cylinder, from which it can be poured out into an open glass vessel, and used as a frigorific agent. It is entitled "K. Olszewski. Transvasement de l'oxygène liquide;" and a brief report on the subject is contained in the *Beiblätter* of Wiedemann, vol. xv. p. 29, under the title "K. Olszewski. Ueber das Giessen des flüssigen Sauerstoffs." That my labours should have thus been passed over in silence is all the more astonishing, because as soon as the above-mentioned *Bulletin* was printed I sent a proof of it to Prof. Dewar; I also forwarded him proofs of my other researches, knowing that they interest him.

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[*] Communicated by the Author.

The apparatus I constructed and described works very well and can be used without danger, so that in October of the same year (1890) I was enabled to obtain 100 cub. centim. of liquid oxygen in the presence of an audience consisting of over 100 students. In the following year, during the Congress of Polish naturalists and physicians in Cracow (July 1891) I obtained 200 cub. centim. of liquid oxygen in the presence of a good many physicists, and showed its peculiar properties; as, *e. g.*, its bluish colour and its absorption spectrum. Subsequently, without having altered my apparatus in any way, I got about 200 cub. centim. of liquid air and used it as a frigorific agent in order to liquefy hydrogen. The construction of my apparatus is very simple, and it can easily be enlarged by using a steel cylinder of the capacity of 300, 400, 500, or more cubic centimetres. The only reason that I have never hitherto employed a steel cylinder of greater capacity than 200 cub. centim., is the circumstance that the quantity of oxygen or air which can be liquefied in this cylinder was quite sufficient for my experiments.

After these remarks, I shall now give a summary of the more important results of my former labours concerning the liquefaction and solidification of gases, and then describe the apparatus I constructed, which serves to obtain great quantities of liquefied oxygen and air; also stating my experiments made in order to liquefy hydrogen, by using large quantities of liquid oxygen or liquid air as frigorific agents.

Summary of the Results of my former Experiments.

In 1883, and for several years following, I liquefied the gases in a strong glass tube, about 30 centim. in length, 14–18 millim. in diameter within, with walls from 3 to 4 millim. thick. Oxygen, nitrogen, atmospheric air, carbon monoxide, nitric oxide, and methane, submitted to the influence of cold in the tube by means of liquid ethylene, boiling *in vacuo* at a temperature of −150° C., were easily liquefied under a pressure not beyond 50 atm. As my experiments proceeded, I published their results in the periodicals I have mentioned; and a detailed description of the apparatus I used in my experiments is contained in Wiedemann's *Annalen der Physik und Chemie*, 1887, vol. xxxi. p. 58, under the title "K. Olszewski. Ueber die Dichte des flüssigen Methans sowie des verflüssigten Sauerstoffs und Stickstoffs." In this apparatus I liquefied all the gases spoken of, in quantities varying from a few to a good many cubic centimetres of liquid, and determined their critical temperatures and pressures, as well as their boiling-points under atmospheric pressure. I succeeded in solidifying four of these gases, viz., nitrogen (6), carbon monoxide (6), nitric oxide (7), and marsh-gas (7), by lowering the pressure to several millimetres of mercury, and determined their freezing-points and the corresponding pressures of solidification. I also showed that liquid oxygen and air boiling *in vacuo* at a pressure of 4 millimetres of mercury do not freeze though their temperatures are lowered to below −211° and −220° C. By diminishing the pressure of solid nitrogen to 4 millimetres of mercury, I obtained a temperature reaching −225° C., *the lowest that has ever been obtained and measured* (6).

With the same apparatus I also made a series of experiments with reference to the liquefaction of hydrogen, submitting it to a pressure reaching 180 atm., and at the same time cooling it down to −211° and even −220° C., by means of liquid ethylene and liquid air boiling *in vacuo* (2). I also showed that the critical temperature of hydrogen is below −220° C. In the same apparatus which served for the liquefaction of hydrogen I liquefied a mixture of two volumes hydrogen and one volume oxygen, and thus obtained a liquid which was in thin layers colourless and transparent (8). I likewise determined the specific gravity of oxygen, nitrogen, and methane at the boiling-points of these gases (15). The same apparatus was also of use for examination of the absorption spectrum of liquid oxygen and air, and showed that liquid oxygen in layers not thicker than 7 millim. absorbs light very strongly; also that it gives, among others, two strong absorption bands, corresponding in position to two absorptions of the solar rays, which are due to the oxygen in the air (13). Using liquid oxygen as a cooling agent, I obtained pure ozone in the shape of a dark-blue liquid, easily and violently exploding, and of which I determined the boiling-point (12).

Besides the above-mentioned gases, I have examined another series with regard to their behaviour at low temperatures, especially those which had not yet been examined in this respect, or which had been examined without success. I first solidified the following gases and determined their melting-points: chlorine (10), hydrochloric acid (10), hydrofluoric acid (11), phosphine (11), arsine (10), stibine (11), ethylene (12), [silicon tetrafluoride* (10)]. Moreover, I determined the boiling-points of ethane (17), propane (17), and hydrogen selenide (19), as well as their critical temperatures and pressures. The following liquids were solidified for the first time by me:—methyl (14), ethyl (14), amyl alcohol (10), ethyl ether (10), carbon bisulphide (14), and phosphorous chloride (PCl_3) (14).

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* Does not melt, but evaporates in solid state.

In order to measure very low temperatures, I used exclusively a hydrogen thermometer: the bulb was plunged in the liquefied gas itself; only exceptionally a few not very low temperatures were measured with the carbon-bisulphide thermometer. Wishing to ascertain how far gas-thermometers may be used to measure very low temperatures, I compared thermometers filled with different gases, and especially the hydrogen thermometer with the nitrogen, oxygen, and nitric-oxide thermometers, immersing them in liquid ethylene, gradually cooled to −151° C. It was proved by this that the three last-mentioned thermometers indicated temperatures not very different from those indicated by the hydrogen thermometer, even at temperatures much lower than the critical temperatures of the corresponding gases.

This experiment proved at the same time that nitric oxide does not change its molecular weight, corresponding to the formula NO, even at a temperature so low as −147° C. Profs. Victor Meyer and Daccomo, disregarding the results of my investigations, performed a similar experiment (Liebig's *Ann. d. Chem.* ccxl. p. 326), but they cooled the nitric oxide with solid carbon dioxide and ether down to −70° C. only.

As, according to my experiments on the liquefaction of hydrogen, its critical temperature lies below −220° C., it may be admitted that its coefficient of expansion does not, even at −220° C., differ much from the coefficient of gases at ordinary temperatures, and that hydrogen is the only body which can be used in a thermometer for measuring very low temperatures. The determinations of the temperatures by measuring the quantity of heat taken away from a given body, a silver ball for instance, is not precise; for, as Zakrzewski * showed, the specific heat of silver changes in the interval of 0° to −100° C. by about 3 per cent.; so that the temperature which is thus determined must differ from the true one to some not inconsiderable extent. Thermoelectric thermometers, or thermometers based upon the variation of the electric conductivity of metals at low temperatures, can be used only in the limits between which they have been compared with the hydrogen thermometer; every extrapolation may lead to great mistakes. An excellent thermometer, based on the alteration of the electric conductivity of a thin iron wire, has been constructed by Prof. Witkowski *, my fellow-worker on the optic properties of liquid oxygen.

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* Bullet. Intern. of the Acad. of Cracow, April 1891, p. 146.

Liquefaction of Large Quantities of Oxygen and Air.

[Description of the apparatus given in the *Bulletin International de l'Académie des Sciences de Cracovie*, June 1890, under the title, "K. Olszewski, Transvasement de l'Oxygène liquide."]

Though I have simplified and improved my former apparatus for liquefying gases to such a degree that I have been able to show the liquefaction of oxygen to a numerous auditory during the lecture, yet it leaves much to be desired as regards the practical application of liquefied gases as cooling agents.

By means of my former apparatus I was able to obtain only small quantities of liquefied gases ; a greater diameter could not be given to the glass tubes used for the purpose, because they would not resist the high pressure which is necessary for liquefaction. Besides this, the use of glass tubes exposed to high pressures is always attended with some danger: it often happens that tubes tested for 60 atm. sometimes burst during the experiment at 40 atm., or even at a lower pressure.

I proved long ago (6) that liquid oxygen is the best cooling agent; for it easily gives the temperature of $-211^{c}\cdot5$ C. if the pressure is lowered to 9 millim. of mercury, and it does not freeze even at the pressure of 4 millim.

To obtain considerably larger quantities of liquid oxygen for the purpose of applying it as a frigorific agent, it was necessary, instead of brittle glass, to use a substance endowed with more resisting-power, even though not transparent, and to find means to pour the liquid oxygen into a glass vessel. My new apparatus excludes the inconveniences of the former one, and renders it possible to preserve the liquid oxygen a longer time under the ordinary atmospheric pressure.

A flask of wrought iron, 5 litres in capacity (such as is used to hold liquid carbon dioxide), containing oxygen under a pressure of 80 atm., is joined by a narrow copper tube to the upper end of a steel cylinder tested at a pressure of 200 atm. This cylinder, having a capacity of 30–100 cub. centim., according to the quantity of oxygen which we wish to liquefy at a time, is immersed in liquid ethylene, of which the temperature may easily be lowered to -140° C. by means of an air-pump. The lower end of the cylinder is joined by a narrow copper tube to a little stopcock, through which the oxygen, liquefied in the cylinder, can be poured down into an open glass vessel kept cool by the surrounding air. Owing to this isolation, liquid oxygen contained in the open vessel evaporates but very slowly; and when after some time its quantity has considerably decreased, a new portion which has been liquefied in the meantime can be led down into the vessel by turning the cock. This may be continued until the store of ethylene serving to cool the cylinder and the amount of oxygen in the iron flask are exhausted. 240 g. of liquid ethylene suffice to keep the oxygen liquid at the atmospheric pressure for half an hour.

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* Bull. Intern. of the Acad. of Cracow, May 1891, p. 188.

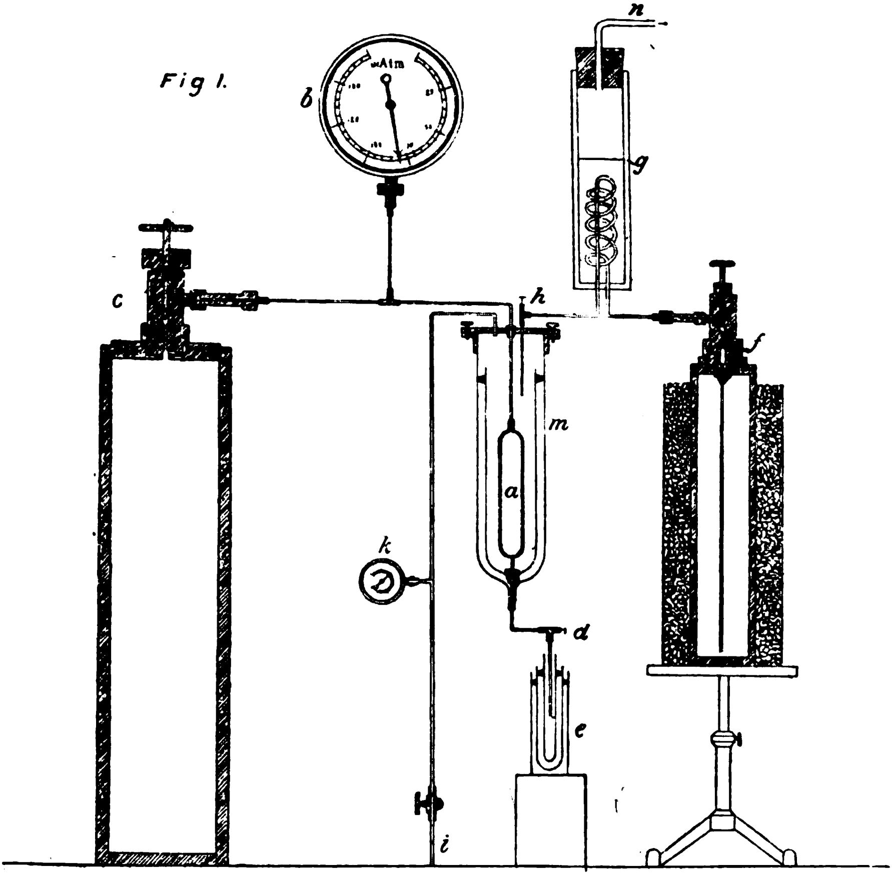
By connecting the glass vessel which contains the liquid oxygen with a good air-pump, its temperature can easily be lowered to −211° C. Thus was solved the problem of liquefying considerable quantities of oxygen without the slightest danger. This decides me to resume my former experiments concerning the liquefaction of hydrogen; and I hope thereby to obtain more successful results.

To this description, which I have given in a literal translation from the above-mentioned *Bulletin International*, I subjoin a diagram (fig. 1) representing a section of my apparatus, which I shall shortly explain. But I must remark that in the same year (1890), when proceeding to my experiments on the liquefaction of hydrogen, I doubled the dimensions of the apparatus without changing anything in its construction. The dimensions that I shall afterwards give refer to the enlarged apparatus.

The steel cylinder *a*, of a capacity of 200 cub. centim., has its upper end connected by means of a thin copper tube with a metallic manometer *b*, and an iron bottle *c* 10 litres in capacity, containing dry oxygen or air under a pressure of 100 atm., the lower aperture of the cylinder *a* being connected by a very thin copper tube with the little cock *d*, which serves to let out the liquefied oxygen or air. The cylinder *a* is placed in a glass vessel *m* with double or treble walls, which serves to receive the liquid ethylene, of which the iron flask *f* is the reservoir. This flask (3 litres in capacity) is shaped like a siphon, and contains about 1 kilog. of liquid ethylene. The ethylene, liquefied and cooled in the flask *f* by means of ice and salt, passes, after the cock is turned, into the condenser *g* filled with a mixture of ether and solid carbon dioxide. To lower the temperature of this mixture −78° C.)

to −100° C., the tube *n* is connected with a smaller double-action pump which at every movement of the piston draws out about 1 litre of gas. When the pressure in the condenser *g* is lowered to 50 millim. Hg, the vessel *m* is connected, by turning the cock *i*, with a large vacuum-pump provided with sliding-valves, and at the same time, by slowly turning the cock *h*, the ethylene, already considerably cooled, is let down into the vessel *m*. The liquid ethylene, on entering the vessel *m*, at first evaporates quickly, and the vapour is forced back into a gasometer by means of the large pump alluded to, and may again be employed as a frigorific agent for a subsequent experiment. Owing to the very great difference between the temperatures of the steel cylinder and the liquid ethylene, the latter does not at first touch the cylinder directly, but is separated from it by a thin layer of vapour, being in

Fig 1.



the spheroidal state: it is only when the cylinder has cooled considerably that the ethylene comes into direct contact with it; a violent boiling of the liquid shows that this has taken place. Henceforward a more abundant stream of ethylene may be poured in until it fills the vessel *m* above the cylinder *a*; afterwards the cock *h* is closed, and the smaller pump which is connected with the vessel *m* by means of the tube *i* must be kept working without interruption, by which the temperature of the ethylene is continually lowered; and when it has fallen below the critical temperature of the gas contained in the flask *c* (oxygen or air), the cock of this flask is slowly opened. The gas enters the cooled cylinder *a* under the pressure indicated by the manometer *b*, and becomes liquid speedily enough, in consequence of which the index of the manometer shows a constant fall; when it becomes stationary, the cylinder *a* is wholly filled with the liquefied gas. When this has been done, the bottle *c* is closed, and by slowly opening the cock *d* the liquefied gas is poured into the glass vessel placed underneath, which is secured from external heat by its triple walls. Whilst the liquid oxygen is being poured from the cylinder *a*, the pressure descends to 20 atm., and remains at this point as long as any liquid oxygen remains in the cylinder: it is only when there is no more that the pressure becomes less than 20 atm. As the liquefied gas comes under the ordinary atmospheric pressure, a considerable part of it resumes the gaseous state, and only half or a third of the liquid remains in the glass vessel after having cooled down to its boiling-temperature. In order to prevent the collected liquid being blown out by the powerful jet, the thin copper tube through which the stream flows is closed beneath, and provided with four lateral openings.

I mentioned above that the temperature of ethylene in the vessel *m* must be lowered by pumping to less than the critical temperature of the gas we wish to liquefy; but it is not necessary to measure the temperature of the ethylene. It is sufficient to measure its pressure. According to my computations (3), the following relation exists between the pressure and the temperature of the liquefied ethylene:—

Pressure. millim. Hg.	Temperature. ° C.
146	−122
107	−126
72	−129 7
56	−132
31	−139
12	−148
9·8	−150·4

The critical temperatures, also according to my reckonings, are: for oxygen −118°·8 C.; for air −140° C.; for nitrogen, −146° C. The pressure of ethylene must accordingly be lowered to 100−40 millim. in order to liquefy oxygen; to liquefy air, to 20 millim., and to liquefy nitrogen, to 10 millim.

The pressure to which ethylene is subjected in the vessel *m* is indicated by the metallic vacuometer *k*, for which in more exact experiments a mercury manometer may be substituted. The pressures I have stated above for ethylene are maximum pressures at which it is still possible to bring about the liquefaction of large quantities of the corresponding gases; but it is generally necessary to take care that the pressure of the liquid ethylene be lowered to the minimum obtainable by the pump serving for the experiment. The more we lower the temperature of the ethylene, the sooner the cylinder *a* is filled with the liquefied gas, and the more liquid we obtain by pouring out the liquefied gas under the ordinary pressure. To lower the temperature of a considerable quantity of ethylene to −146° or −150° C., which temperature is absolutely necessary for the liquefaction of large quantities of air and nitrogen, a large air-pump with rapid and powerful action is required. When in 1890 I used a smaller pump, which drew out two litres of gas at each complete double stroke, I could only liquefy oxygen in the described apparatus; but when in the following year I brought from Burckhard's factory, Basle, an excellent sliding valve-pump, six times larger than the preceding one, and working with great speed and perfection, I was enabled in the same apparatus easily to obtain at once 200 cub. centim. of liquid air. It is true that I never tried to liquefy nitrogen in large quantities, but I believed it unnecessary, taking into account my former experiments with nitrogen (6). I had already examined the properties of liquid and solid nitrogen, and showed that the use of liquid nitrogen as a frigorific agent is of no greater advantage than that of oxygen or air. However, considering that by using both of my pumps the pressure of ethylene in the vessel *m* is easily lowered to 10 millim. and the temperature to −150° C., I can decidedly affirm, that all so-called permanent gases, except hydrogen, may be liquefied in my apparatus. When we want to obtain such a considerable rarefaction of ethylene, the compressing tube of the larger pump must be connected with the exhausting tube of the smaller one, whereby the effect of the larger pump is exceedingly increased.

It need hardly be said that the processes connected with the liquefaction of large quantities of gases, as the liquefaction of ethylene in the cylinder *f*, the charging of the cylinder *c* with oxygen or air, and the working of both the larger and smaller pump, must be accomplished not by hand, but by means of a gas-motor of 1–3 H.P.

The indispensable condition for such experiments to be successful, is the purity of the gases to be liquefied; the liquid carbon dioxide, used as a frigorific agent, must be free from moisture; the ethylene, oxygen, and air must be completely dry and free from carbonic acid. A small amount of carbon dioxide in oxygen or air renders these gases turbid and opaque when liquefied: a slight quantity of moisture may freeze and stop up the narrow tubes which join together the component parts of the apparatus, and thus frustrate the experiment, prepared with so much trouble. In order absolutely to purify oxygen and air from water and carbon dioxide, there must be put into the bottle *a*, before it is charged, 1 kilog. of potassium hydroxide in thin sticks, that will in a few days completely absorb the moisture and carbonic acid which may be produced whilst the gas is being forced into the flask, in consequence of the action of the condensed oxygen on the leather piston of the pump.

The quantities of liquid oxygen and air I got by means of the apparatus described were quite sufficient for carrying out my experiments on the liquefaction of hydrogen and the examination of the optical properties of liquid oxygen, which I shall shortly describe. On that account I did not think it necessary to increase the dimensions of the apparatus (which, however, it would have been easy to do), the more so because, after having liquefied the first 200 cub. centim. of oxygen or air, the operation may be repeated every 15 minutes, on an equal quantity of gas, as long as the store of liquid ethylene suffices, and the pressure in the bottle *c* does not fall below 60 atm.: in this case other cylinders, containing the whole charge of the corresponding gas, should take the places of *c* and *f*.

I now pass to the description of the experiments I have executed by means of the apparatus described, either by myself or working in conjunction with Prof. Witkowski.

On the Absorption Spectrum and the Colour of Liquefied Oxygen.

[Notice published in German in the ***Bulletin International de l'Académie de Cracovie***, January 1891, and in Wiedemann's ***Annalen***, 1891, vol. xlii. p. 633.]

In my earlier investigations* I found four absorption-bands in the spectrum of liquid oxygen, corresponding to the wave-lengths 628, 577, 535, and 480. Messrs. Liveing and Dewar *, who at a later date examined the absorption spectrum of gaseous oxygen in a long steel tube under a strong pressure, found the same four absorption-bands in the visible part of the spectrum, and, besides them, in the utmost red two others, corresponding to the lines *A* and *B* of the solar spectrum, which were also observed by Egoroff and Janssen.

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* ***Wiener Akademie Berichte***, xcv. p. 257.

The apparatus I have described enabled me to repeat my former experiments and to examine more exactly the absorption spectrum of a thicker layer of liquid oxygen in the utmost red.

The liquid oxygen was poured out of the liquefying apparatus into a thin-walled glass tube, the lower end of which was soldered and closely fixed into three glass vessels one outside of the other, to preserve it from external heat. The column of oxygen was 30 millim. thick and about 50 millim. deep. In this glass tube the oxygen remained at its boiling temperature (—181°·4 C.) under atmospheric pressure, in sufficient quantity for the experiment, during more than half an hour, though it was strongly heated by a Drummond's lime-light, concentrated on it by means of a collecting-lens: this light was used to produce the absorption spectrum. In examination of the spectrum I used a universal spectroscope of Krüss, with a prism of Rutherford. Besides the four known absorption-bands, the experiment also proved the existence of a fifth band, corresponding to the solar line *A*: it is somewhat blurred, but can be seen distinctly enough if a red glass is put between the source of light and the slit in the spectroscope. This band appeared feebler than the absorption-bands which correspond to the wave-lengths 628, 577, and 480, but stronger than the absorption-band at 553. With this relatively slight dispersion, the band *A* could of course not be decomposed into lines. And this time too I was unable to perceive any absorption corresponding to the solar *B*.

The experiments in 1883 made out liquid oxygen to be a colourless fluid, for but small quantities of it were then obtained. Since then I have several times observed that oxygen, when liquefied in wider tubes about 15 mm. thick, appears of a bluish colour. During my experiments already alluded to, in which for the first time a relatively considerable quantity of liquid oxygen was collected in a glass vessel, its bluish colour appeared quite distinctly. The oxygen was prepared from potassium chlorate and manganese dioxide; to ascertain that it contains no traces of ozone from which the bluish colour might be derived, it was carefully tested for that substance. Paper moistened with potassium iodide and starch, exposed for several hours to the action of the oxygen used, was not coloured at all ; and when the oxygen was made to pass through a solution of potassium iodide and starch the result was the same. It remained for several weeks in an iron flask, in contact with solid potassium hydroxide, and was by this means completely purified from carbonic acid, vapour of water, and chlorine. After these experiments, there is no doubt that liquid oxygen, seen in layers of about 30 millim., possesses a distinctly bluish colour. This colour is, moreover, quite in agreement with the absorption spectrum of oxygen. It was rather strange that a colourless liquid—as it was hitherto thought to be—should give such a pronounced absorption spectrum, in which the absorptions in orange, yellow, and red are preponderant ; but after the bluish colour of liquefied oxygen was proved, this apparent contradiction no longer exists.

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* Phil. Mag. [5] xxvi. p. 286 (1888.)

I may conclude with a word or two about the colour of the sky. There exist so many hypotheses on that point, that I scarcely venture to add one more. But the simplest theory, in my opinion, would be to ascribe that colour to the principal component part of our atmosphere, which—at least in a liquid state—is blue.

On the Critical Pressure of Hydrogen.

[These researches were published in Polish, in the Reports of the Cracow Academy 1891, vol. xxiii. p. 385; a short German abstract therefrom was printed in the *Bullet. Intern.* of the same Academy. The following description is taken from the first-named source, and is explained by figs. 2 and 3.]

In my former researches, undertaken in 1884 and 1885, I showed that hydrogen cannot be liquefied even by employing the lowest obtainable temperatures and a high pressure, reaching to 190 atm. ; and that it is only during the sudden expansion from a high pressure that a greater or less trace of liquefaction can for an instant be seen. This depends on the temperature of the frigorific medium, as well as on the initial pressure of expansion. As cooling agents there were employed :—oxygen boiling under atmospheric pressure ($t = -181^\circ \cdot 4$) and *in vacuo*, reaching to 9 millim. ($t = -211^\circ \cdot 5$) ; also air boiling under atmospheric pressure ($t = -191^\circ \cdot 4$) and *in vacuo* at 10 millim. ($t = -220^\circ$), as well as nitrogen boiling under atmospheric pressure ($t = -194^\circ \cdot 4$) and *in vacuo* at 60 millim. ($t = -213^\circ$).

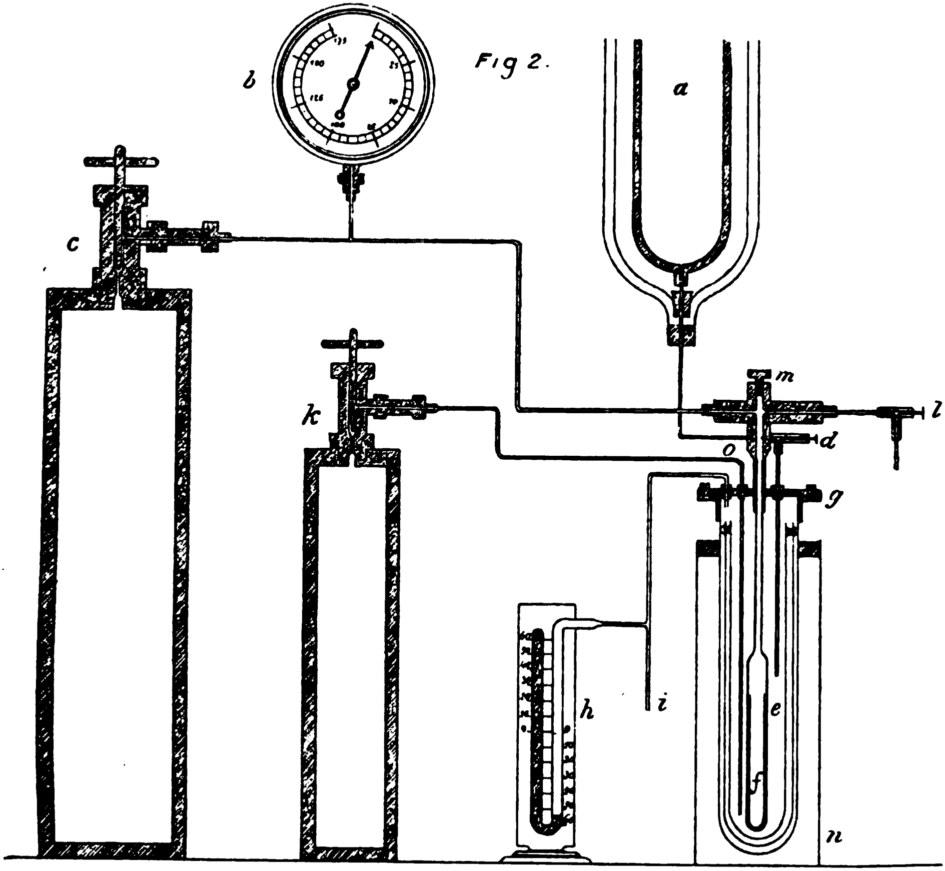
I also showed that nitrogen, boiling *in vacuo* at 4 millim., gives the lowest possible temperature, reaching −225°, but that it can be used as a cooling agent only as far as −213°, for at lower temperatures, under pressures below 60 millim. Hg, it solidifies to a snowy opaque mass, which is a bad conductor of heat. It follows that liquid oxygen and air are the best means to obtain the lowest temperatures, for neither of them solidifies at all, even at the lowest pressures, and neither possesses transparency. I had already used these cooling agents in my former attempts to liquefy hydrogen; I then exhausted all possible means of obtaining the lowest temperatures without obtaining the desired results; for the temperature of −220°, *i. e.*, the lowest which can be produced by means of liquefied air, proved to be above the critical temperature of hydrogen.

On repeating my former experiments I had no hope of obtaining a lower temperature by means of any cooling agent, but I hoped that the expansion of hydrogen would be more efficacious, on account of the larger scale on which the experiment was made.

The quantity of the frigorific medium, viz., of liquid air or oxygen, did not exceed 2–3 cub. centim. under atmospheric pressure, and became considerably less by the use of the vacuum; accordingly, the glass tube which contained hydrogen was only 2 millim. in internal diameter. The phenomenon of liquefaction, or rather of sudden ebullition of hydrogen which appeared in the tube during the expansion, lasted only a fraction of a second, and required a relatively sudden but not complete expansion. The hydrogen, cooled by its expansion below its critical temperature, was at once heated in so narrow a tube to the temperature of the surrounding frigorific medium.

In the subjoined diagram (fig. 2) *a* represents the lower end of the steel cylinder, serving to liquefy oxygen or air; this cylinder is enclosed in a glass vessel (double, if oxygen be employed; triple, if liquefied air) which serves to receive liquid ethylene. The cylinder *a* is a component part of the apparatus represented in fig. 1, and is therefore marked with the same letter; but it was increased for these experiments to 200 cub. centim. in capacity. The glass tube *f* is destined for the liquefaction of hydrogen; the external diameter of this lower and wider part is 11 millim., the internal diameter is 7 millim. Within it I place a short glass tube, with very thin walls 6 millim. in diameter; it serves to isolate from the warmer walls of the larger tube the hydrogen which is considerably cooled by its expansion. The tube *f* is placed in a larger glass tube *e*, with thin walls, measuring 30 millim. in internal diameter, and serving to receive the liquid oxygen under atmospheric pressure. The tube *e* is surrounded by two

Fig 2.



others, of greater and greater diameter, and hermetically closed above with a brass plate *g*. The whole apparatus is hermetically placed in a larger glass cylinder, with calcium chloride at the bottom, serving to dry the enclosed air. The top of the tube *f* is connected with the manometer *b* and the iron bottle *c*, containing absolutely pure and dry hydrogen, under a pressure of 150 atm.; the cock *l* serves to let the hydrogen out of the tube *f*, thus producing the expansion; through the upper end of the tube *f*, which is closed with the screw *m*, a thermoelectric junction may be introduced, if it be required to measure the temperature of the hydrogen at the moment of expansion. I performed the experiment as follows:—

By opening the cock *d* I let the liquid oxygen, contained in the steel cylinder *a*, into the vessel *e*; a part of the oxygen, which thus returned into the gaseous state, escaped with violence through the tube *i*; another was cooled down to its boiling-point (−181°·4 C.) and collected as a bluish liquid in the tube *e*, to a height of 6–7 centim., so that the wider part of the tube *f* was plunged in liquid oxygen. I afterwards closed the cock *d* and joined the tube *i* to the pump, by slowly opening a cock, which is not represented in the figure; the mercury manometer *h* indicated the pressure of the liquid oxygen in the vessel *e*. Liquid oxygen behaves very quietly in the vessel *e* under atmospheric pressure, boiling quickly but uniformly on being pumped: if we do not reach very low pressures, the oxygen, after cooling according to the lowered pressure, boils again quietly. But if the pressure falls below 10 millim. (or less), the oxygen boils irregularly, the liquid is thrown up, and shortly disappears. To avoid this I introduced into the vessel *e* a capillary glass tube *o*, the lower end of which reaches to the very bottom of the vessel *e*, the upper end is connected with the iron cylinder *k*, containing dry hydrogen under a pressure of several atmospheres. During the pumping of the oxygen the cock of the cylinder *k* is little by little opened, and a slow stream of hydrogen is let through the liquid oxygen; by this means the liquid oxygen is constantly and easily removed, and it boils quietly, even if the pressure falls to 4 millim.

When the manometer *h* indicated a pressure of 10–4 millim. I introduced hydrogen into the tube *f*, by slowly opening the cylinder *c*, until the pressure became 140 atm., as indicated by the manometer *b*. When the hydrogen in the tube *f* has come down to the temperature of the cooling agent, I little by little produced expansion, by opening the screw-cock *l*. The phenomenon of hydrogen ebullition, which was then observed, was much more marked and much longer than during my former investigations in the same direction (3, 4). But even then I could not perceive any meniscus of liquid hydrogen.

I have remarked in these experiments, that with a slow expansion the phenomenon of sudden ebullition always appears under the same pressure, no matter how great the initial pressure may be, provided that value be not too low. So that by expansions made, beginning with the pressures of 80, 90, 100, 110, 120, 130, 140 atm., the phenomenon described constantly appeared at 20 atm.; but if the initial pressure was 70, 60, and 50 atm., the ebullition appeared at a lower and lower pressure, viz., approximately at 18, 16, and 14 atm. I repeated the same experiment a good many times, and always obtained the same results. These experiments bring me to the conclusion, that the 20 atm. at which the ebullition of hydrogen always appears represents its critical pressure. If hydrogen, cooled by means of liquid oxygen, boiling *in vacuo*, to the temperature −211° C., which, we may suppose, is several degrees above the critical temperature of hydrogen, is submitted to a slow expansion from a high pressure, its temperature is lowered to the critical temperature, hitherto unknown. If the initial pressure is high enough—in my experiments it was above 80 atm.—then, by means of a slow expansion, the temperature of hydrogen sinks to its critical value, before its critical pressure is reached, and then liquid hydrogen will appear the moment we lower the pressure to its critical value. But if the initial pressure is too low, a slow expansion cools the hydrogen to the critical temperature only after the critical pressure has been passed: the lower the initial pressure is the greater is the expansion needed to cool the hydrogen below its condensing temperature. We may thus explain the changing pressures, corresponding to the phenomenon of ebullition or instantaneous liquefaction in the case of expansion from an insufficient initial temperature. And if the initial pressure is still lower, the instantaneous liquefaction will not appear at all.

To ascertain the truth of this statement I performed two series of analogous experiments with gases, the critical pressures and temperatures of which are accurately known, viz., with oxygen and ethylene. The critical temperature of oxygen is, according to my former researches, −118°·8 C., its critical pressure is 50·8 atm. In the same apparatus which I used for the experiments with hydrogen I cooled oxygen by means of ethylene boiling under atmospheric pressure (−102°·5), then to a temperature 16·3 degrees below the critical temperature of oxygen, and subjected it to a slow expansion, beginning with different initial pressures, from 40 atm. up to 100 atm. The ebullition of oxygen always appeared at a pressure of about 51 atm., provided the initial pressure was not lower than 80 atm.: at the same time there also appeared a meniscus of liquid oxygen. As the initial pressure became lower and lower, so did the ebullition pressure too.

The critical temperature of ethylene according to Prof. Dewar is 10°·1, the critical pressure 51 atm.; my own determinations of the same quantities yielded results agreeing well with the above-cited, viz., 10° C. and 51·7 atm.

I made similar experiments with ethylene, using the apparatus of Cailletet; one series at a temperature of 17° C., another at 27°; then at temperatures, which were first 7°, then 17° higher than the critical temperature of ethylene. During the first series of experiments, the ebullition of ethylene, and at the same time the meniscus, appeared constantly in consequence of a slow expansion at a pressure of about 51 atm., if the initial pressure was 70, 80, 90, 100, and 110 atm. During the second series of experiments the ebullition appeared at the same pressure, if the initial pressure was 100, 110, 120, and 130 atm. In proportion as the initial pressure was lowered—in the first series below 70 atm., in the second below 100 atm.—the ebullition pressure was lowered too. I must, however, mention that in the apparatus of Cailletet, in which I made the experiments with ethylene, the conditions of ebullition of any gas by expansion are much less advantageous than in the apparatus described above.

Hence it follows that the determination of critical pressures by means of expansion is possible, even if the gases have a temperature which is several or many degrees higher than their critical temperature. This dynamical method of determination of critical pressure is really of no advantage if applied to the other gases, for these pressures may be more easily and precisely determined by the vanishing of the meniscus; but with hydrogen it is the sole possible way to determine not only its critical pressure, but also its critical temperature.

On repeating these experiments in November 1891 I used liquid air, boiling under a pressure of 4–10 millim., as a cooling agent, and obtained the same results, with the only difference that the ebullition of hydrogen on expansion appeared still more distinctly and persisted somewhat longer.

The reason for which it has not been hitherto possible to liquefy hydrogen in a static state, is that there exists no gas having a density between those of hydrogen and of nitrogen, and which might be for instance 7–10 (H=1). Such a gas could be liquefied by means of liquid oxygen or air as cooling agent, and be afterwards used as a frigorific menstruum in the liquefaction of hydrogen.

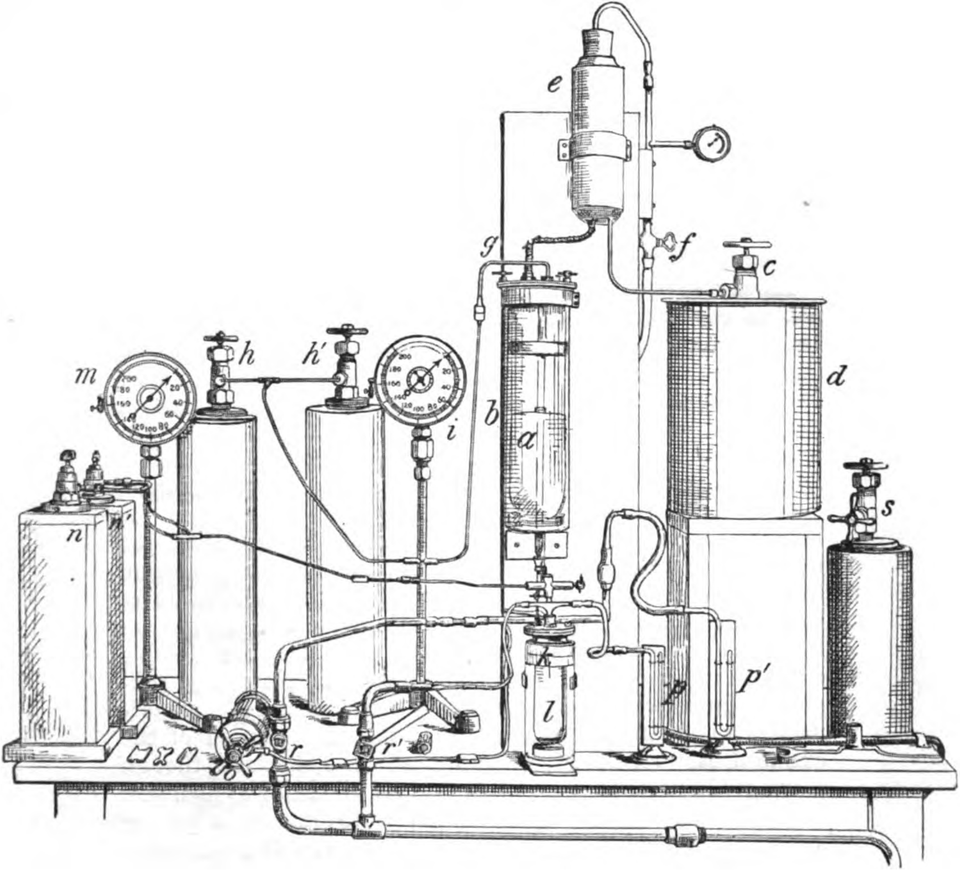
The subjoined figure 3, taken from the original, represents my apparatus for liquefying large quantities of oxygen and air, connected with the apparatus serving to determine the critical pressure of hydrogen. The following brief description will help to understand the figure:—

(*a*) The steel cylinder, 200 cub. centim. in capacity, for the liquefaction of oxygen or air.

(*b*) The glass vessel with triple walls, serving to receive liquid ethylene under diminished pressure.

(*c*) The iron flask, 3 litres in capacity, containing liquid ethylene, under high pressure.

Fig. 3.



(*d*) A zinc vessel with ice.

(*e*) The condenser, for cooling ethylene by means of ether and solid carbon dioxide.

(*f*) The cock connecting the condenser with the small pump.

(*g*) The cock serving to let liquid ethylene into the vessel *b*.

(*h h′*) Iron flasks, 10 litres in capacity, containing oxygen or air under a pressure of 100 atm., connected by means of a tube with the manometer *i* and the cylinder *a*.

(*k*) The glass vessel with triple walls, serving to receive liquid oxygen or air under atmospheric pressure.

(*l*) The glass tube, plunged in liquid oxygen or air, serving to liquefy hydrogen, connected with the manometer *m* and iron cylinders *n n'*, containing hydrogen under a pressure of 150 atm.

(*o*) Iron flask containing hydrogen under the pressure of several atmospheres, which passes through the liquid oxygen in the vessel *k*, when its pressure is diminished.

(*p p'*) Mercury manometers, serving to measure the pressure of ethylene and liquid oxygen, contained in the vessels *b* and *k*.

(*r r'*) Cocks serving to connect the vessels *b* and *k* with the large pump.

(*s*) Iron cylinder, containing liquid carbon dioxide.

As my experiments on the liquefaction of hydrogen do not at all confirm those of M. Pictet, made at Geneva in 1879, I requested Dr. Krzyżanowski to examine whether the glaring discrepancies between my experiments and M. Pictet's might not be explained by impurities contained in the hydrogen he used. And indeed Dr. Krzyżanowski (24) proved that, if potassium formate be heated with potassium hydroxide, hydrogen cannot be obtained free from moisture, even in the most advantageous case, which occurs when the latter is in excess; and that if these substances are employed in the proportion given by M. Pictet, that is with potassium formate in excess of what is required by the calculation of molecular weights, we get by heating them a sample of hydrogen containing not only water but also considerable quantities of carbon monoxide and dioxide. Now these substances, interfering with the purity of the hydrogen experimented on by M. Pictet, were doubtless the ground of the extraordinary results M. Pictet described, and which, though glaringly improbable, are cited in nearly all chemical manuals. Perhaps this remark of mine will contribute to a proper appreciation of M. Pictet's experiments respecting the liquefaction and solidification of hydrogen; perhaps it will suggest to the author (who has now established a laboratory in Berlin with the special purpose of obtaining very low temperatures) that he might, with advantage for science, control and rectify the results of the work he performed in 1879.

On the Optic Properties of Liquid Oxygen.

[These investigations were made in collaboration with my friend Prof. Witkowski, and were published in the Reports of the Cracow Academy and in the *Bulletin International*, October 1891 and June 1894.]

As far back as 1887 I discovered a very remarkable and powerful selective absorption of light in the liquefied oxygen.

It was desirable to obtain some numerical data as regards the absorbing power for the several bands. For this purpose we made use of the spectrophotometer of Glan. The liquid oxygen was contained in the innermost tube, provided with a flat bottom, of the apparatus shown in the annexed figure (fig. 4, taken from the *Bulletin International*, October 1891).

Fig. 4.

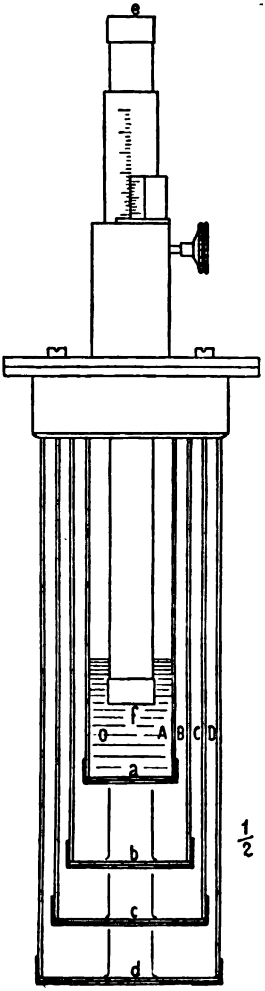
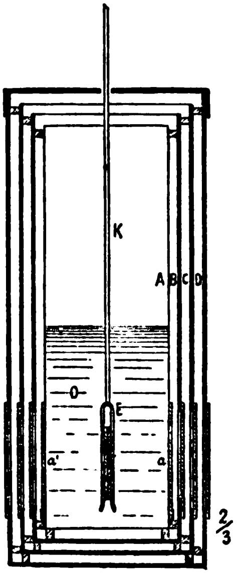


Fig. 5.



The thickness of the liquid could be varied to a known degree by screwing up and down the tube *ef*, closed at both ends by plane glass plates, and provided with a millimetre division.

So far as the accuracy of photometric measurements under such difficult conditions could be relied upon, we found a proportion of light varying between 84 and 89 per cent., transmitted by a layer of oxygen 1 millim. in thickness in the most intense part of the yellow-greenish band ($\lambda=577$ to $\lambda=570$). The corresponding average number for the red band ($\lambda=630$ to $\lambda=638$) was 88 per cent.

In the same pamphlet we described a method of determining the coefficient of refraction of liquid oxygen and gave results for sodium light. The most suitable method for the purpose proved to be that of total reflexion. The liquid is contained in a thin iron parallelepipedon A (see fig. 5), provided with plane glass windows, and protected by several varnished pasteboard boxes of similar form containing some phosphoric anhydride. A double glass plate, composed of two carefully selected plane bits of glass, separated at the corners by small pieces of mica (thickness about 0·006 millim.) and cemented at their obliquely-ground borders by means of fish-glue, is immersed in the oxygen. The double plate is rigidly conected with the axis of a divided circle. A similar arrangement has been employed by Ketteler in some of his investigations on the refraction and dispersion of water (Wiedemann's *Annalen,* vol. xxxiii.). It is therefore unnecessary to enter into particulars as regards the mode of observation and calculation of results. A first series of observations gave the value 1·2235 of the coefficient for sodium light, in very close agreement with a result found by Messrs. Liveing and Dewar by means of the prism method. Later determinations of the same constant by myself and Prof. Witkowski, made with the view of ascertaining the dispersion of liquid oxygen (*Bulletin International,* July 1894), yielded a rather smaller result (1·2226) as a mean of five distinct measurements. At the same time we found $n=1{\cdot}2213$ for $\lambda=670{\cdot}5$, and 1·2236 for the wave-length 535 $\mu\mu$. Anomalous dispersion, specially sought for, could not be detected.

Besides these researches I have made (partly by myself, partly in collaboration with Prof. Witkowski) certain hitherto unpublished experiments concerning the intensity of chemical energy at low temperatures; I mention them here to complete the list of my investigations. They refer chiefly to two substances, viz. liquid ethylene and oxygen, under the influence of agents which combine with these substances at the usual or at a higher temperature. Ethylene, boiling under atmospheric pressure ($-102^{\circ}{\cdot}5$ C.) was submitted to the action of chlorine and bromine. The action was feeble, but in both cases I obtained products of combination ($C_2H_4Cl_2$ and $C_2H_4Br_2$) in considerable quantity.

The possibility of preparing relatively large quantities of liquid oxygen in open vessels at atmospheric pressure gave us an opportunity to examine the chemical properties of this interesting substance more closely. We ascertained first the exceedingly feeble chemical affinity of liquid oxygen. A piece of metallic sodium in contact with it showed no change in its metallic brilliancy; a hardening of the substance, in consequence of its very low temperature, being apparently the only effect produced. This might have been anticipated, considering that every trace of moisture had been frozen away. Potassium acted similarly to sodium.

But when the reaction of oxidation with light and heat phenomena had already begun, the low temperature (−181°·4) is not able to cool the burning substance to such a degree as to interrupt the reaction. For instance, a piece of ignited wood immersed in liquid oxygen takes fire just as in gaseous oxygen; a steel spring burns and spreads sparks of burning iron, which in this experiment burst the glass vessel of oxygen, and the liquid oxygen was consequently spilt on the table, giving thus the interesting sight of liquid drops rolling and jumping about in a perfectly spheroidal state.

In this connexion, as I had (in 1891) large quantities of liquid oxygen, my friend Prof. Kreutz performed a series of experiments on the behaviour of coloured substances at very low temperatures, and showed that many of them (HgS, HgI_2, I, &c.) become much brighter at −181°·4.

From this summary of researches, as well as of dates, it follows that the first apparatus serving to produce large quantities of the liquefied so-called permanent gases, with the solitary exception of hydrogen, was constructed by me. This apparatus can be enlarged at will by increasing its parts, but without changing anything in its construction, so that it might be used to obtain liquefied gases in factories should they at any time prove of practical utility. By means of this apparatus I obtained as large quantities of liquid gases as I wanted; and they were used for the first time on a large scale as cooling agents (for instance, in my attempts to liquefy hydrogen), or as an object of scientific researches (the absorption spectrum of liquefied oxygen, its coefficient of refraction, &c.)

The experiments of Prof. Dewar are merely the repetition,

Gas.	Critical temperature.	Critical pressure.	Boiling-point.	Freezing-point.	Freezing-pressure.	Density at boiling-point.	Colour of liquefied gas.
Hydrogen (H_2)......................	below −220°	20 atm.					
Nitrogen (N_2)	−146°	35 „	−194·4°	−214°	60 mm. Hg.	0·885	Colourless.
Oxygen (O_2)	−118·8°	50·8 „	−181·4°	......	......	1·124	Bluish, absorbs light powerfully.
Air	−140°	39 „	−191·4°	......	......	......	Nearly colourless.
Carbon monoxide (CO)	−139·5°	35·5 „	−190°	−207°	100 mm. Hg.	......	Colourless.
Nitric oxide (NO)	− 93·5°	71·2 „	−153·6°	−167°	138 „		
Methane (CH_4)	− 81·8°	54·9 „	−164°	−185·8°	80 „	0·415	Colourless.
Ozone (O_3)............................	......	......	−106°	......	......	......	Dark blue, easily exploding.
Ethane (C_2H_6)	+ 34°	50·2 atm.	− 93°	at −151° still liquid.	......	......	Colourless.
Propane (C_3H_8)	+ 97°	44 „	− 45°		......	......	Colourless.
Ethylene (C_2H_4)	+ 10°	51·7 „	−102·5°	−169°	......	......	Colourless.
Chlorine (Cl_2)	......	......	......	−102°	......	.. ...	Yellow-orange.
Hydrochloric acid (HCl).........	.. ...	......	......	−116°	......	......	Colourless.
Hydrofluoric acid (HFl)	......	......	......	− 92·3°	......	......	Colourless.
Phosphine (PH_3)	......	......	− 85°	−133°	......	......	Colourless.
Arsine (AsH_3)	......	......	− 55°	−119°	......	......	Colourless.
Stibine (SbH_3)	......	......	− 18°	− 91·5°	......	......	Colourless.
Hydrogen selenide (H_2Se)	+138°	91 atm.	− 41°	− 68°	......	......	Colourless.
Silicon tetrafluoride ($SiFl_4$)......	......	......		about −102°	......	......	Does not melt.

and confirmation of these researches, most of which were published several years before his corresponding investigations. His work is really original only as to the magnetic properties of liquid oxygen: that which is not borrowed from my researches is a development of ideas struck out by another—as, for instance, the experiments on electrical resistance at low temperatures, which were begun by Clausius, continued by Cailletet and Bouty, and brought ten years ago by my former fellow-worker, the late Prof. Wróblewski*, to the temperature of the freezing-point of nitrogen, then several degrees below the temperature attained in the experiments of Messrs. Dewar and Fleming, who, it is true, extended their examination to various metals, alloys, and non-metals. But the execution of these labours meets with no difficulty; for the method of getting large quantities of liquefied gases is now generally known.

In the table opposite (p. 210) I have set down the most important numbers, obtained as stated in my former experiments, concerning the liquefaction and solidification of gases.

List of my Researches, of which I have specified the most important Results in the foregoing Summary.

All my researches were at first published in the Polish language, in the publications of the Cracow Academy of Sciences; I afterwards published an excerpt of each of them in French and German. The present list contains only French and German papers, as being accessible to students of every nationality. The numbers enclosed in brackets in the preceding summary have reference to the ordinal numbers of the following list.

1. K. Olszewski. Essais de liquéfaction de l'hydrogène.—*Comptes Rendus*, vol. xcviii. p. 365 (1884).
2. ——. Nouveaux essais de liquéfaction de l'hydrogène, solidification et pression critique de l'azote.—*C. R.* vol. xcviii. p. 913.
3. ——. Température et pression critique de l'azote. Température d'ébullition de l'azote et de l'éthylène sous de faibles pressions.—*C. R.* vol. xcix. p. 133 (1884).
4. ——. Température et pression critique de l'air. Relation entre la température de l'air et la pression de l'évaporation.—*C. R.* vol. xcix. p. 184 (1884).
5. ——. Relation entre les températures et les pressions du protoxyde de carbone liquide.—*C. R.* vol. xcix. p. 706 (1884).

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* *Comptes Rendus*, ci. p. 161.

6. K. Olszewski. Température de solidification de l'azote et du protoxyde de carbone; relation entre température et la pression de l'oxygène liquide.—*C. R.* vol. c. p. 350 (1885).
7. ——. Liquéfaction et solidification du formène et du deutoxyde d'azote.—*C. R.* vol. c. p. 940 (1885).
8. ——. Sur la production des plus basses températures.—*C. R.* vol. ci. p. 238 (1885).
9. ——. Bestimmung der Dichte und des Ausdehnungscoëfficienten des flüssigen Sauerstoffs.—*Anzeiger der Akad. der Wissensch. in Wien*, 1884, nr. ix.
10. ——. Bestimmung der Erstarrungstemperatur einiger Gase und Flüssigkeiten.—*Monatshefte für Chemie, Akad. d. Wissensch. in Wien*, vol. v. p. 127 (1884).
11. ——. Erstarrung des Fluorwasserstoffs und des Phosphorwasserstoffs, Verflüssigung und Erstarrung des Antimonwasserstoffs.—*Sitzungsberichte d. Akad. in Wien*, vol. xciv. p. 209 (1886).
12. ——. Bestimmung des Siedepunktes des Ozons und der Erstarrungstemperatur des Aethylens.—*Ibidem*, vol. xcv. p. 253 (1887). Also Wiedemann's *Annalen*, vol. xxxiii. p. 570 (1888).
13. ——. Ueber das Absorbtionsspectrum des flüssigen Sauerstoffs und der verflüssigten Luft.—*Ibidem*, vol xcv. p. 257 (1887). Also Wiedemann's *Annalen*, vol. xxxiii. p. 570 (1887).
14. S. Wróblewski and K. Olszewski. Ueber die Verflüssigung des Sauerstoffs, Stickstoffs und Kohlenoxyds.—Wiedemann's *Annalen*, vol. xx. p. 243 (1883).
15. K. Olszewski. Ueber die Dichte des flüssigen Methans sowie des verflüssigten Sauerstoffs und Stickstoffs.—*Ibidem*, vol. xxxi. p. 58 (1887).
16. ——. Ueber das Absorbtionsspectrum und über die Farbe des flüssigen Sauerstoffs.—*Ibidem*, vol. xlii. p. 663 (1891).
17. ——. Sur l'éthane et propane liquides.—*Bulletin International de l'Académie des Sciences de Cracovie*, January 1889, I.
18. ——. Appareil pour liquéfier et solidifier les gaz appellés permanents et pour étudier leur spectre d'absorbtion.—*Ibidem*, January 1889.
19. ——. Sur les propriétés physiques de l'acide selénhydrique soumis à une basse température et à la pression.—*Ibidem*, February 1890.
20. ——. Transvasement de l'oxygène liquide.—*Ibidem*, June 1890.
21. ——. Ueber den kritischen Druck des Wasserstoffs.—*Ibidem*, May 1891.
22. Olszewski and A. Witkowski. Propriétés optiques de l'oxygène liquide.—*Ibidem*, October 1891.
23. —— ——. Sur la dispersion de la lumière dans l'oxygène liquide.—*Ibidem*, July 1894.
24. K. Krzyżanowski. Sur la liquéfaction et la solidification de l'hydrogène dans les experiences de M. Pictet.—*Ibidem*, January 1889.

XX. *Mirrors of Magnetism.*

By SILVANUS P. THOMPSON, *F.R.S., and* MILES WALKER[*].

OUR knowledge of Electric Images is based almost entirely upon mathematical deduction. It would be difficult to satisfactorily demonstrate their properties by experiment. We are content to take the elegant geometrical proofs that Lord Kelvin has given us, and corroborate these physically at points where the conclusions are within reach of experiment. The subject, therefore, is one of purely theoretical interest, but so beautifully does it elucidate difficult problems in Electrostatics that it remains the continual delight of text-book writers.

Magnetic Images, on the other hand (apart from one or two investigations by the same great master), are entirely neglected, and yet these are much more likely to be practically utilized in the near future than their electrical analogues. It may be in questions of dynamo and instrument shielding, or it may even be in the solution of that commercial problem, the testing of the magnetic properties of iron *en masse*.

The existence of magnetic images is suggested by considerations altogether apart from the mathematical.

If we take a solenoid of wire through which a current is flowing and place its end against a large plate of iron, we eliminate the effect of that end upon the distribution of the field about the coil, and so obtain a field on one side of the plate of a shape the same as if the coil were continued to double its length. If we place the coil with its end against a mirror (fig. 1), we see it reflected in the mirror so that it appears to be double its real length. Thus the iron plate gives us magnetically an image of the coil analogous to the optical image produced by the mirror, geometrically identical indeed with the optical image, virtual and erect.

If a large iron plate is placed at each end of the coil the field will be the same as if the coil were infinitely long. We know that two mirrors, facing each other, one at each end of the coil, would give it the appearance of stretching away to infinity in both directions (fig. 2).

Of course these optical effects could only be perfectly obtained if the mirror were a perfect reflector; and to include all possible points of view it would have to be infinitely large. So the magnetic effects could only be perfectly obtained if the plates were perfectly permeable and infinitely large. Observe that we are only considering the effect at a point *in front* of the mirror and in front of the iron plate.

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[*] Communicated by the Physical Society: read November 23, 1894.

Behind, that is to say on the side opposite the coil, there is no effect in either case.

Fig. 1.

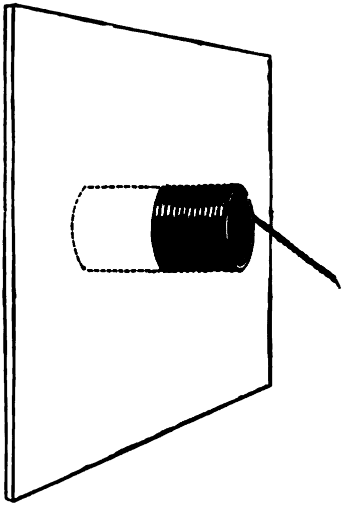
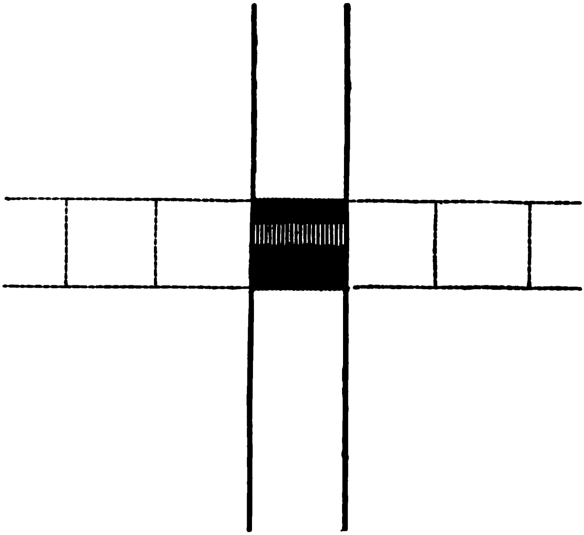
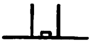
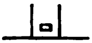
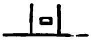
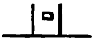
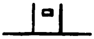
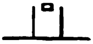
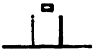
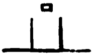
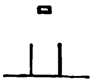


Fig. 2.



It was thought interesting to ascertain how far effects of this kind could be obtained in practice, using an ordinary iron plate somewhat less than that required for the perfect case. For this purpose two similar solenoids were wound, 5 centim. long and 4 centim. mean diameter, the winding at the ends being exposed so that it could be put up close to the iron. A search-coil of 100 turns, about 1½ centim. in diameter, was mounted so that it could be fixed at different positions relatively to one of the solenoids, which was then placed upon the iron plate* and upon the other solenoid alternately. A current of constant value was turned on and off in each position of the solenoid, and the throw on a ballistic galvanometer in the circuit of the search-coil observed. The following table, giving the throw of the needle for different positions of the search-coil, shows how perfectly the iron plate mirrored the magnetism of the solenoid. The discrepancy in the figures arises more from errors of observation than anything else.

Position of Search-coil.	Throw when coil on coil.		Throw when coil on iron.	
	Make.	Break.	Make.	Break.
	236	236	236	235
	235	235	234	234
	230	230	230	229
middle 	227	227	228	227
	204	202	204	202
end 	129	126	129	127
	69	67	69	68
	41	41	41	41
	24	24	24	23

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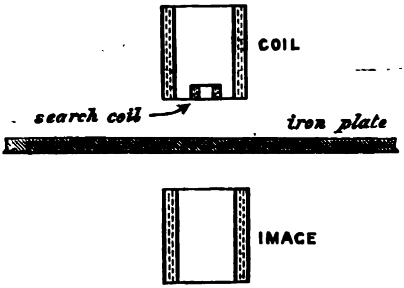
* The iron plate was ordinary boiler-plate ¼ inch thick, size 3 feet by 2 feet.

The first position in the above table is the most important, as the coil is placed in a part of the field that experiences the greatest change by the presence or absence of the iron plate, the difference being that between 236 and 129. If the search-coil could have been placed so that its centre was at the very end of the solenoid, the throw ought to be just one half of what it would be with the coil continued to double its length. This was found to be so when the solenoid was placed on the other solenoid, but could not be tried with the iron as part of the search-coil protruded.

The experiment was then made of lifting the solenoid step by step a little distance from the iron plate, when it was found that the presence of the iron plate had the effect of producing an image of the coil receding an equal amount behind the plate.

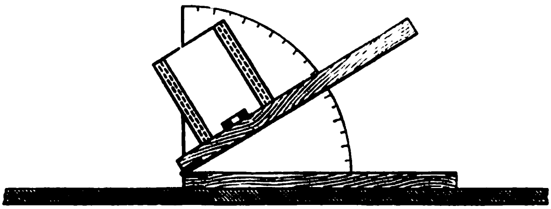
Fig. 3.



A larger search-coil was placed in different positions outside the solenoid; and in all positions on which any readable throw of the needle could be obtained, it was found that the iron plate gave an effect almost exactly the same as an equal solenoid in the position of its image.

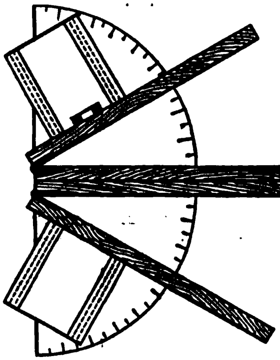
In order to try the effect of tilting the solenoid, it was mounted on a strip of wood hinged to another, the angle between them being fixed by a clamp (fig. 4.) This was then placed alternately on the iron plate and against a similar

Fig. 4.



hinged strip upon which the other solenoid was placed, the angle of inclination being the same for both solenoids (fig. 5).

Fig. 5.



The angle was altered step by step from 0 to 90 degrees, and in all cases the iron plate produced the same effect as its image within limits not greater than those shown in the previous table. It was, however, only when the solenoid was placed at the end of the hinged strip nearest the iron plate that readings of any value could be obtained, as small dislocations in the position of the coil laterally were apt to produce changes of reading comparable with those due to considerable changes in angle. At distances greater than 5 centim. the iron had very little effect. The search-coil during these experiments was moved about to different positions both inside and outside the solenoid, preference being given to the most sensitive positions.

Then the effect of differently-shaped solenoids was tried. A long narrow one and a wide flat one were used with similar effects, so far as they could be measured.

There is a difference between the magnetic reflexion of an iron plate and the optical reflexion of a mirror in the following respect: an optical image has those of its lines which are at right angles to the mirror reversed while those parallel to the mirror are not reversed. For instance, if we hold a magnet with its north end pointing from us and towards a mirror, the optical image of it will have its North end pointing towards us (fig. 6). But in the case of a magnetic image this is inversed: the magnetic image has its South end pointing towards us. In fact the reflexion of a North end is a South end. If, however, we look at the reflexion of the currents flowing in the solenoid instead of at the sign of the pole of the solenoid, we see that laws of the optical case hold good for the magnetic case. The image (fig. 7) of a current flowing in any direction in a plane parallel to the mirror is another current flowing parallel to the first and towards the same part.

Fig. 6.

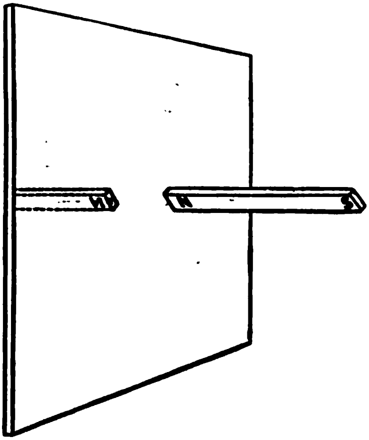


Fig. 7.

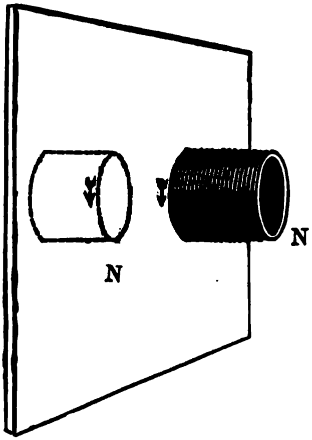
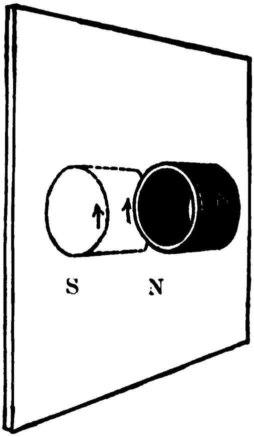


Fig. 8.



A North pole viewed from the front is equivalent to a lævo-cheiral circulation of current. The image of this pole turned towards the mirror is, to the spectator, a dextro-cheiral circulation, or a South pole. The same is true if, as in fig. 8, the solenoid has its axis parallel to the plane of the mirror.

In order to try some effects with an isolated pole, a solenoid, 2 metres long and 1·5 centim. mean diameter, was uniformly wound with twelve turns per centimetre of a suitable wire. When a current of 15 amperes was passed through this a pole of a strength of about 40 units (C.G.S.) was obtained, and this might be regarded as an isolated pole at distances not greater than 30 centim. from it. It was found that bringing an iron plate within a few centimetres of this pole produced very nearly the same effect upon the field as would have been produced by bringing up a pole of opposite sign to a point at double the distance.

Fig. 9.

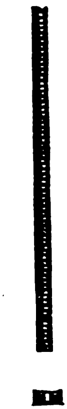
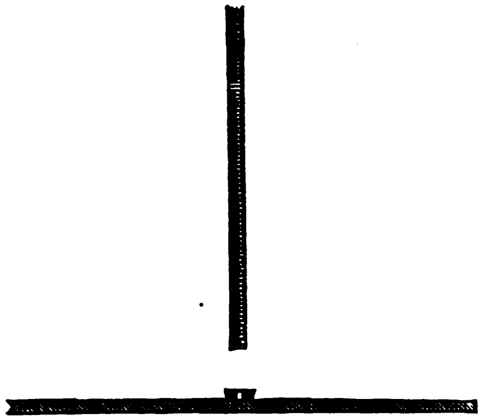


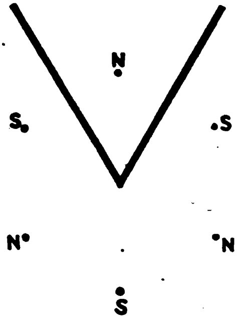
Fig. 10.



The field close to the iron plate ought to have been exactly twice as strong as if no iron plate were there. This was found to be so within the limits of error of observation (about 3 per cent.) when the pole was within 6 centim. of the iron plate. As the distance was increased the throw of the needle became too small to be accurately read, and the field being extremely weak the susceptibility of the iron would be very low.

It was this weakness of the field (for one could not consider the pole as a point except at distances exceeding 10 centim.) that spoilt some experiments on kaleidoscope effects. One can conceive that if the laws of reflexion hold good between a magnetic pole and a sheet of iron, it ought to be possible, by means of several sheets of iron, to build up a magnetic kaleidoscope by which the effect of a great number of magnetic poles could be produced from a single pole. The idea of a magnetic kaleidoscope was suggested by Lord Kelvin many years ago, but it is doubtful whether it has ever been successfully carried out. If, for instance, two plates of susceptible material are inclined to each other at an angle of 60 degrees, and the North pole of a magnet placed evenly between them, one would expect to get between the plates exactly the same distribution of field as if there were six poles, three norths and three souths, spaced alternately and evenly round the line of intersection of the plates. It may, however, be said to those who would care to try this experiment, that they must use a point pole of much greater strength than 40 units, or plates much more susceptible than iron if they hope to be at all successful.

Fig. 11.

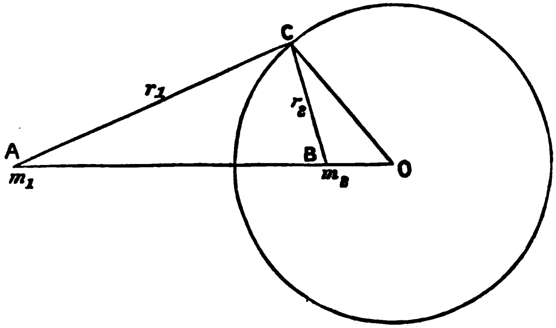


The close connexion between the effect of an iron plate magnetically and that of a mirror optically naturally makes us ask what would be the effect of a curved plate? Would it give magnified or diminished images like a concave or convex mirror, and what would be the position of these images with regard to the object?

If we take the case of spherical curvature, and consider the iron as being infinitely susceptible, the answer to these questions can be determined theoretically from the laws of magnetic potential. All the formulæ relating to electric images already known are applicable to magnetic images.

If we consider two points A and B at which are placed two poles respectively, of the strengths $+m_1$ and $-m_2$, the

Fig. 12.



magnetic potential at a point C due to m_1 is $\frac{m_1}{r_1}$ where $r_1 = \text{AC}$, and that due to $-m_2$ is $-\frac{m_2}{r_2}$ where $r_2 = \text{BC}$.

The total potential at C is therefore $\frac{m_1}{r_1} - \frac{m_2}{r_2}$.

If we choose C at a point of zero potential, we have

$$\frac{m_1}{r_1} - \frac{m_2}{r_2} = 0;$$

that is to say

$$\frac{m_1}{m_2} = \frac{r_1}{r_2}:$$

but $\frac{m_1}{m_2}$ is a constant; therefore, if we take C at the points of zero potential $\frac{r_1}{r_2}$ will always be constant. But if a point moves so that $\frac{r_1}{r_2}$ remains constant it moves on the surface of a sphere, therefore the equipotential surface of value zero is in the form of a spherical shell. If O be the centre of the sphere, it follows from a well-known property of a circle that

$$\frac{AO}{OC} = \frac{r_1}{r_2} = \frac{m_1}{m_2}.$$

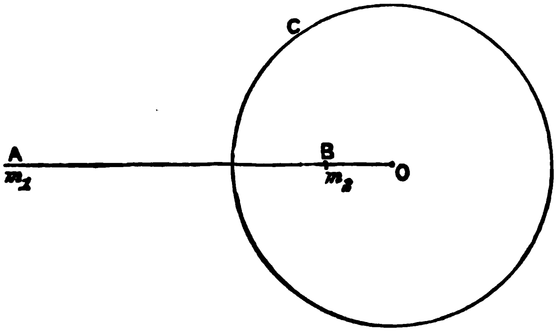
If, therefore, we are given m_1 we can find from the equation

$$m_2 = m_1 \frac{O}{AO},$$

the strength of pole m_2 which when placed at B will give zero potential on a given spherical shell.

Now consider a magnet pole $+m_1$ (fig. 13) brought up to

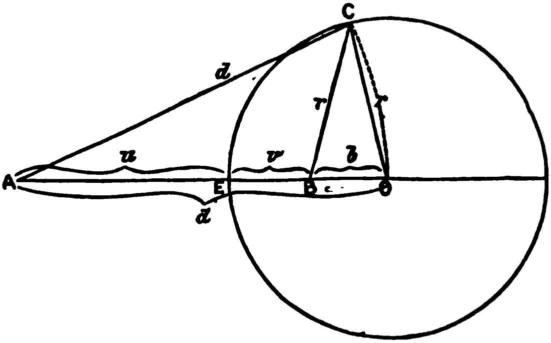
Fig. 13.



a point A near a sphere of very susceptible material whose radius is large as compared with the distance between A and its surface, so that we may neglect the potential of the sphere due to m_1 in dealing with the potential of points in the field we are considering, and so that we may take the surface of the sphere as an equipotential surface of practically zero value*. The distribution of the field outside the sphere will be the same as if no sphere were there, but instead a pole of strength $-m_1\frac{\mathrm{OC}}{\mathrm{AO}}$ were placed at B. We may say that the sphere acting like a convex mirror has given a diminished image at B.

We can find the position of B by the following construction :—Describe the arc OC (fig. 14) with A as a centre, and

Fig. 14.



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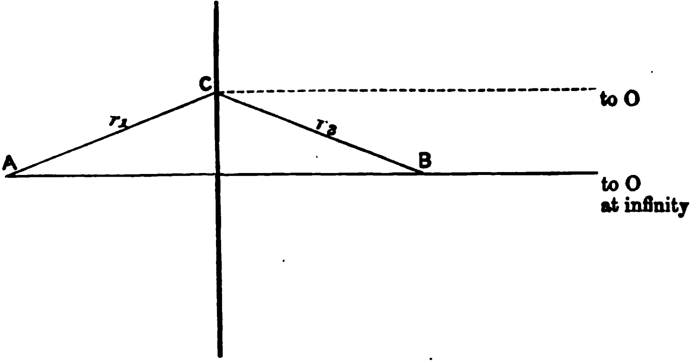
* [*Note added after reading of Paper.*—At this point our original paper contained the following remark as a footnote :—"If the magnetic object is large, or is far removed, then besides the image as above defined it is necessary to take into account the raising of the potential of the whole sphere, which would be represented by another image at the centre." As some discussion took place on this point after the reading of this paper, it may be well to deal further with the matter. The case is then analogous to the case of an electric charge q brought up to an insulated conducting sphere having no previous charge. Lord Kelvin, in a paper dated July 7th, 1848, has shown that the effect on external points of the charge residing on the surface of such a sphere is the same as the effect of a charge $-\frac{r}{d}q$ at B (fig. 14), and a further charge of $+\frac{r}{d}q$ at the centre O. His reasoning being applicable to the magnetic case, we see that the image of a North pole at A consists of a doublet having a South pole situated at B of strength $m_1\frac{r}{d}$ and a North pole also of the strength $m_1\frac{r}{d}$ situated at the centre O. Now any magnetic object such as a solenoid will have a South pole as well as a North pole, and if the object is small compared with the size of the sphere, both North and South may be taken as equidistant from the centre, and their images at the centre will therefore neutralize each other, and we have left the image that is considered in the text. If the object is large as compared with the size of the sphere, then in both the magnetic case and the optical case there is a confusion of images.]

then describe the arc OB with C as a centre, B being on the line AO. The condition that $\frac{r_1}{r_2}$ shall be constant for all points on the circumference is that $\frac{\mathrm{OC}}{\mathrm{BO}}$ shall be equal to $\frac{\mathrm{AO}}{\mathrm{OC}}$, and this is seen to be true from the similarity of the triangles ACO and COB.

If we had any number of magnetic points outside the sphere each would have its virtual image inside the sphere; thus any form of magnet, such as a solenoid carrying a current, would also have its image.

It is easy to see that the experiments above mentioned with a large iron plate can be explained in this way. For if we may consider the plate as part of an infinite sphere:

Fig. 15.



in this case $\frac{\mathrm{AO}}{\mathrm{OC}}=1$; therefore $\frac{m_1}{m_2}=1$; therefore $m_1=m_2$: and further $\frac{r_1}{r_2}=1$; therefore $r_1=r_2$.

To assimilate to optical formulæ let us now express the relations in terms of the distance of object and image respectively from the pole E of the mirror, and write $\mathrm{AO}=d$; $\mathrm{BO}=b$; $u=\mathrm{AE}=d-r$; $v=\mathrm{BE}=r-b$ (fig. 14). Now

$$\frac{d}{r}=\frac{r}{b}, \text{ by similar triangles.}$$

This may be written

$$\frac{u+r}{r}=\frac{r}{r-v};$$

whence

$$\frac{1}{u} + \frac{1}{r} = \frac{1}{v}.$$

The well-known optical mirror formula for a spherical mirror differs from this in having $\frac{2}{r}$ instead of $\frac{1}{r}$.

In order that a magnetic image as at B in fig. 14 should be produced by a magnetic object at A, and with the relative strengths m_2 and m_1, not only must the reflecting surface pass through the point E such that

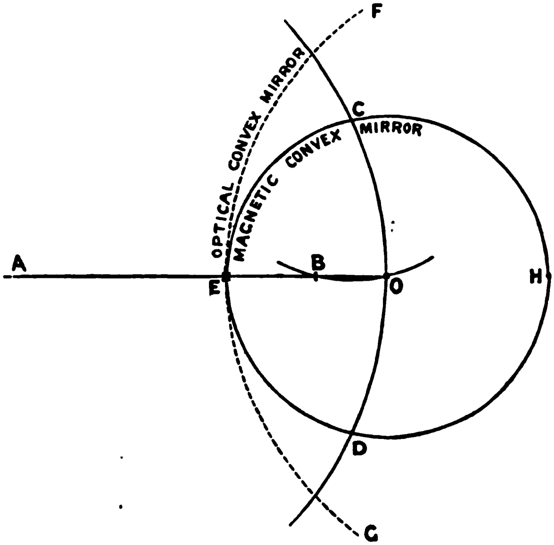
$$\frac{\mathrm{AE}}{\mathrm{BE}} = \frac{m_1}{m_2},$$

but the curvature of the magnetic mirror is defined by the condition previously laid down that

$$\frac{\mathrm{AO}}{\mathrm{CO}} = \frac{m_1}{m_2} \text{ also.}$$

Now the optical mirror which will give at B the image of A, and have its middle-point situated at E (as defined by the former of these conditions) will not have O for its centre.

Fig. 16.



In fact it will be a spherical surface having half the curvature or twice the radius. If (fig. 16) the dotted circle FEG be drawn with centre H, we have the sectional view of the optical convex mirror which will give the same position of image as the magnetic convex mirror shown by the circle CED.

In conclusion, it may be remarked that the construction of fig. 14 affords a new and simple graphic method of finding the position of optical images, by the device of using the auxiliary circle whose diameter is the radius of the spherical surface.

XXI. *Notices respecting New Books.*

The Scientific Basis of Analytical Chemistry.

Die wissenschaftlichen Grundlagen der Analytischen Chemie. Elementar dargestellt von W. Ostwald. (Leipzig: Wilhelm Engelmann. 1894.)

It has been so long the custom with a certain class of teachers in this country to regard analytical chemistry as synonymous with chemical science that the very title of this book will come as a surprise. Prof. Ostwald, in the present little volume of 187 pages, has attempted to present the subject of chemical analysis in a popular form and in a new way. Whether he has succeeded in his objects in his own country it is difficult to say, but so far as English chemists are concerned the book is certainly not likely to achieve popularity: first, because it is not arranged in accordance with our examinational notions of chemical analysis; and, secondly, because it bases the analytical properties of the elements and their compounds on a theory which has not found general acceptance in this country, viz. the theory of ionic dissociation. But in calling attention to these two points we are really bestowing praise upon the work; because any novelty of treatment in such a well-worn field is to be cordially welcomed, and all attempts to approach the subject from a different scientific aspect to that generally adopted are bound to help in the "depolarization" of cut and dried dogmas which are so baneful to true progress in science.

Of the two parts into which the book is divided, the first, consisting of five chapters, deals with theory, and the second, consisting of eight chapters, deals with applications. The theoretical part, where concerned with the ordinary operations, is lucidly put together, and forms quite pleasant reading as compared with the purely cookery-book kind of directions that the student in this country is expected to follow. We doubt much whether the average "certificated teacher" knows that there is any scientific theory behind the processes which he has been drilled into carrying out. It is in the fourth chapter, under the heading *Die chemische Scheidung*, that the new theory of solutions is first broached, and from that part onwards everything connected with the subject is treated of from the point of view of ionic dissociation. Whether this view is accepted or not, it must be conceded that Prof. Ostwald has made out a good case in support of its applicability to the ordinary processes of analysis. The key-note is struck on p. 47 in the following extract, which we paraphrase:—

"In aqueous solutions of electrolytes the ions are generally partly combined and partly uncombined. In neutral salts the uncombined portion is by far the greater, and is in fact the more in preponderance the more dilute the solution. The properties of dilute salt-solutions are consequently determined, not so much by the properties of the dissolved salt as such or by the combined ions, but rather by the properties of its free ions. Through this conception the analytical chemistry of saline matter (*salzartigen Stoffe*) at once undergoes an enormous simplification: it is not the analytical properties of salts as a whole, but only those of their ions which have to be established. Supposing that 50 anions and 50 kations are given, these can form with each other 2500 salts; and supposing these salts to possess individual reactions, the properties of 2500 kinds of matter must be individually enunciated. But since the properties of the dissolved salts are simply the sums of the properties of their ions, it follows that the knowledge of $50+50=100$ cases is sufficient to predominate over the whole possible number of 2500 cases. As a matter of fact, analytical chemistry has long made use of this simplification. It has long been known, for example, that the reactions of the copper salts are the same with respect to copper, whether we examine the sulphate, nitrate, or any other salt; the scientific formulation and the cause of this behaviour have, however, been reserved for the dissociation theory."

Any polemically disposed chemist might feel inclined to traverse the last statement, but we have said enough to show that we have at any rate a work on chemical analysis which can in reality be called a new work. It is worthy of the most careful study, and its pages will be found interesting both by veterans and novices; an opinion which is tantamount to the highest praise that can be bestowed upon a book devoted to a subject in which there has been practically no scope for a new departure since the time of Liebig.

XXII. *Intelligence and Miscellaneous Articles.*

ON THE CHANGE OF LENGTH IN SOFT IRON WIRE PLACED IN A UNIFORM MAGNETIC FIELD. BY B. ROSING.

To the Editors of the Philosophical Magazine.

Gentlemen,

In No. 224 (vol. xxxvii.) of your esteemed Magazine was published a paper by Mr. Nagaoka on "Hysteresis attending the Change of Length by Magnetization in Nickel and Iron." Since the autumn of 1891 I have been investigating the same question, and the results I have now obtained agree in general with those of Mr. Nagaoka. Some discrepancy between our observations may be explained as due to a divergence in the conditions of experiment [*]. The method I used consisted in the application of interference-fringes and sensitive lever. Its sensitiveness was nearly the same as that in the method of Mr. Nagaoka: one division of the microscope scale corresponding to a change of length $=11\times10^{-7}$ cm. Influence of temperature effects was compensated by a peculiar bimetallic suspension of the sensitive lever.

The results I have obtained are given in the following Table, where H represents magnetic force (C.G.S. units), $\frac{\delta l}{l}$ elongation per unit of length of my iron wire [†], and I its magnetization.

H (C.G.S.).	$\frac{\delta l}{l}\times10^9$.	I (C.G.S.).
67·4	−137·1	1495
50·5	−107·0	1495
33·7	− 62·2	1448
25·3	− 28·6	1395
16·9	− 1·7	1283
13·5	+ 13·6	1206
8·4	+ 24·3	1142
5·1	+ 29·5	1065
3·4	+ 29·5	1012
1·7	+ 26·6	965
0	+ 21·7	920
− 1·7	+ 13·9	683
− 3·4	+ 3·8	312
− 5·1	+ 7·8	− 418
− 6·7	+ 12·2	− 559
−10·1	+ 15·1	− 900
−13·5	+ 11·3	−1060
−16·9	+ 4·1	−1107
−25·3	− 21·4	−1219
−33·7	− 45·1	−1272
−50·5	− 88·8	−1378
−67·4	−124·7	−1454

Theoretical views permit us to suppose the following correlation between $\frac{\delta l}{l}$ and corresponding values of H and I —

$$\frac{\delta l}{l}=a\mathrm{I}^2+b\mathrm{IH}+c\mathrm{H}^2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

My friend Mr. Weinberg has kindly calculated the coefficients of this formula by the method of least squares. These are as follows:—

$$a=4{\cdot}4834\times10^{-14}, \quad b=-365{\cdot}023\times10^{-14}, \quad c=3015{\cdot}31\times10^{-14}.$$

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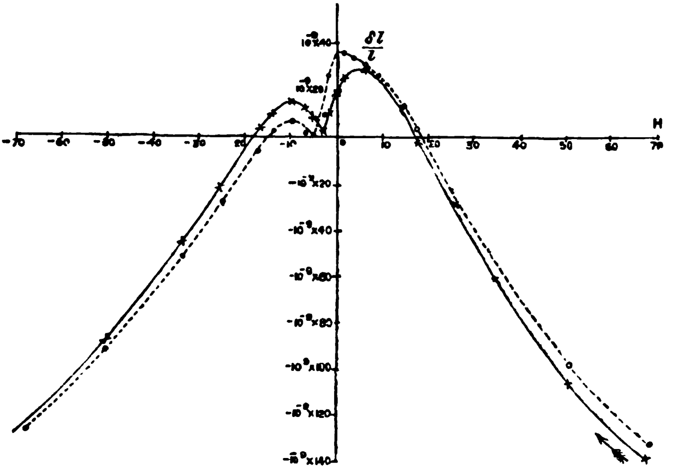
[*] The iron bars of Mr. Nagaoka were comparatively thick and short, the ratio of their length to their diameter was not greater than 70, whereas my wire had for this ratio about 494. This wire was moreover stretched.

[†] Mean of several sets of observations.

The dotted curve on the accompanying figure represents the relation between $\frac{\delta l}{l}$ and H calculated by the formula (1), and the plain curve the results of observations.



The mean difference between the values of $\frac{\delta l}{l}$ observed and calculated is equal to about $6{\cdot}7 \times 10^{-9}$ or to 3 per cent. of the maximum value. This difference is too great for an exact formula, but as *a first approximation* the formula (1) may be accepted. Thus I may set forth the results of my investigation in the following form:—

A soft iron wire, 39·5 *cm. long and* 0·083 *cm. thick, with a longitudinal stress of* 380 $\frac{gr.}{mm.^2}$ *and placed in a magnetizing solenoid* 86 *cm. long and* 3·85 *cm.*^{2} *in mean section, by cyclic magnetization shows a change of length, which may be expressed, as a first approximation, by the formula*

$$10^9 \times \frac{\delta l}{l} = 0{\cdot}000044834 \times I^2 - 0{\cdot}00365023 \times IH + 0{\cdot}0301531 \times H^2,$$

where $\frac{\delta l}{l}$ *is elongation per unit of length,* I *magnetization, and* H *magnetic force.*—Abstract of a paper published in the *Journal of the Russian Physico-Chemical Society,* xxvi. pp. 253-264.

Physical Laboratory,
University of St. Petersburg, Russia.

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[FIFTH SERIES.]

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XXIII. *Some Experiments with Alternating Currents.* By ALBERT GRIFFITHS, *M.Sc., Berkeley Fellow of Owens College, Manchester*[*].

THIS paper embraces experiments on certain actions produced by an alternating current when it passes through the coil or coils of a galvanometer, and investigations of a peculiarity noticed by Lenard, viz., that the resistance of bismuth in a strong magnetic field, when measured with an alternating current and a telephone, is greater than when measured with a steady current and a galvanometer; in addition there are some theoretical considerations.

As mentioned by Dr. Schuster in Phil. Mag. vol. xlviii. 1874, p. 340, it is found that if an alternating current and constant current combined go through the coils of a galvanometer, the deflexion of the needle is greater than that produced by the constant current alone.

In my experiments, an induction-coil supplied with Kohlrausch's apparatus for the determination of electrolytic resistance was used as the source of the alternating current, the interrupter of which was replaced, initially, by a tuning-fork which gave 128 complete vibrations per second.

The galvanometer employed was one of Edelmann's: there is a pair of coils on each side of the needle which can be placed at various distances from the needle; the coils can also be rotated as a whole about a vertical axis passing through the centre of the needle. The needle consists of a steel ring, suspended with the plane of the ring vertical.

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[*] Communicated by Prof. A. Schuster, F.R.S.

Chrystal gave a very complete explanation of the phenomenon in Phil. Mag. p. 401, vol. ii. 1876; his explanation depends on the assumption—no doubt correct—that the magnetization of a steel needle can be caused to vary by a magnetic field, however small.

Suppose that, through any cause, the needle makes an angle with the plane of the galvanometer coils: owing to the fact that a needle is most readily magnetized lengthwise, that component of a magnetic field parallel to the needle produces a decided change in the magnetization lengthwise, whilst the action of the field in any other direction is relatively small. It is unnecessary to go into details, but it is found, on examination, that the field, with lines at right angles to the plane of the coils, which tends to increase the angular deflexion increases the magnetization of the needle: on the other hand, the field which tends to diminish the angular deflexion diminishes the magnetization of the needle. Hence in the case of alternations the currents that tend to increase the deflexion give greater impulses than those in the other direction, and in consequence the angular deflexion of the needle is increased. The same would happen if the needle were not magnetized.

Since the change in the magnetization of the needle will vary approximately as the strength of the alternating current, and the action on the needle varies as the product of the change and the strength of the alternating current, it follows that the action on the needle will vary approximately as the square of the alternating current. This I proved indirectly by using an alternating current of constant strength, and placing the coils at various distances from the needle, having previously determined the relative sensibilities of the galvanometer for the various distances with a steady current.

Still following Chrystal, it is obvious that if a magnetized steel sphere, or any steel body bounded by a surface of revolution whose axis is that of suspension, be suspended, the superimposed magnetization will always be parallel to the lines of force in the field, and hence there will be no turning moment due to this cause.

I suspended a magnetized steel sphere in place of the ordinary needle, and was surprised to find that when the angular displacement of the magnetic axis with respect to the coils was in one direction, an alternating current *increased* the deflexion: when the angular displacement was in the other direction, an alternating current *diminished* the deflexion.

A magnetized steel ring behaved in a similar manner; in this case I proved experimentally (indirectly) that the action on the needle varied approximately as the square of the alternating current; also on resuspending the ring so as to make what was previously the lower side the upper one, the direction of the deflexion was reversed. An explanation did not strike me at the time of experimenting, but perhaps the true explanation is that, owing either to some defect in homogeneity or in geometrical shape, the direction most susceptible to magnetization was inclined at an angle to the magnetic axis. Suppose, for example, that the angle were 45°: since the angle which the direction most susceptible to magnetization makes with the plane of the coils is increased by an alternating current, it is obvious that the magnetic axis could be rotated 45° in either direction before there was a change in the direction of the deflexion produced by the alternating current.

Although, undoubtedly, the phenomena described above are almost entirely due to magnetic causes, it was thought advisable to try some experiments with a copper (non-magnetic) ring.

It must be mentioned that the Edelmann galvanometer was supplied with dampers which consisted of two hollow metal cylinders capable of movement to various distances from the needle. The copper ring was suspended with a diameter vertical and capable of rotation about that diameter; when the dampers were pushed in as far as possible, the angle between the plane of the ring and the plane of the coils was increased by an alternating current; when the dampers were drawn out, the angle was diminished. These repulsions and attractions are no doubt caused by the interactions of the original alternating current in the galvanometer coils, and the induced currents, of various phases, in the copper ring and dampers.

The copper ring was sawn across, so that the circle was no longer complete; the action on the ring of an alternating current in the galvanometer coils was now almost negligible.

A steel ring was sawn across, so that the circle was no longer complete, and then magnetized and suspended with a diameter vertical. An alternating current produced a powerful action on the suspended needle, although no induction-currents of any importance could exist.

In the preceding experiments I was troubled with slight irregularities which I attributed to imperfections in the alternating current, and I attributed the imperfections, perhaps erroneously, to slight irregularities in the make and break.

The interruptions in the primary circuit were caused by a platinum point leaving a mercury surface which was covered with methylated spirit. The spark seemed to me to be an erratic factor, and I endeavoured to get rid of it by employing a resistance as a shunt across the spark-gap, by employing a condenser as a shunt, and in particular by a method of Differential Winding, which was only a partial success, described by S. P. Thompson in 'The Electromagnet and Electromagnet Mechanism.'

The method of Differential Winding diminishes the spark on break, but certainly does not eliminate it; as the action of the arrangement is of some interest, I have given a full explanation of its construction and behaviour in Addendum I.

The device for preventing sparking which acted the best, and which I think is a new one, consists in the use of electrolytic cells or small batteries placed as a shunt across the spark-gap.

I first used electrolytic cells, the platinum plates of which were about 1 in. by $\frac{5}{8}$ in., and dipped in dilute or strong sulphuric acid.

The explanation is that the cells polarize, and on making the gap an E.M.F. is introduced opposed to the E.M.F. of the battery, so that the current rapidly diminishes, decomposing the liquid and doing chemical work.

I may mention, incidentally, that the rapid make and break of current through the electrolytic cells disintegrated the surface of either the positive or negative plates (I did not observe which) and brought platinum into suspension, in a very finely divided state, throughout the liquid.

I tried plates of gas-charcoal in dilute H_2SO_4; these did not act so well as the platinum.

I tried lead plates in dilute H_2SO_4; these acted quite as well as the platinum plates, and are of course cheap.

When the above-mentioned device was employed there was no trouble with the mercury; in fact the little sparking there was seemed to purify rather than contaminate the surface.

Having now had some experience with alternating currents, I was recommended to examine some of Lenard's experiments[*] on the electrical resistance of bismuth in a magnetic field with constant and alternating currents.

The telephones and bridge employed were those which are used for the determination of electrolytic resistances by Kohlrausch's method; the bridge-wire is wound on a cylinder.

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[*] Wied. *Ann.* xxxix. p. 619 (1890).

To eliminate any possible errors due to the self-induction of the bridge-wire, the resistance of the standard arm was always varied until the reading of the bridge was not far from the middle of the wire.

I no longer employed a tuning-fork as interrupter, but used an apparatus discussed in Addendum II., which enabled me to obtain any number of breaks per second up to 500.

To explain the fact, discovered by himself, that a bismuth wire in a strong magnetic field has apparently a higher resistance when measured with a telephone and an alternating current than with a galvanometer and constant current, Lenard frames the bold hypothesis that it is not the frequency of by far the greater part of the alternating current that has to do with the increased resistance, but accidental (so to speak) oscillations with a frequency of about 10,000.

With the bismuth spiral in a strong field absolute silence is never obtained in the telephone, but there is a decided minimum noise of a nondescript character.

No differences of resistance could be detected with frequencies between 60 and 500.

It is well known that an alternating current tends to travel along the surface of a conductor, especially when the conductor is magnetic; the result is that the resistance for an alternating current is greater than for a steady one.

Let l be the length of a straight wire, R the resistance to steady currents, $p/2\pi$ the frequency of vibration, μ the magnetic permeability for circumferential magnetization, R′ the resistance to alternating currents; then if $\frac{p^2l^2\mu^2}{R^2}$ is small,

$$R' = R\left\{1 + \frac{1}{12}\frac{p^2l^2\mu^2}{R^2} - \frac{1}{180}\frac{p^4l^4\mu^4}{R^4}\right\} \text{ approx.*},$$

or

$$R' = R\left\{1 + \frac{1}{12}\frac{p^2l^2\mu^2}{R^2}\right\} \text{ roughly,}$$

$$= R\left\{1 + \frac{1}{12}\frac{p^2\mu^2}{r^2}\right\},$$

where r = resistance per unit length.

In the case of a copper wire 1 millim. in diameter, where $\mu = 1$, the increase of resistance with an alternating current of frequency 10,000 equals about one tenth.

The formula becomes unworkable when $\frac{p^2l^2\mu^2}{R^2}$ is large; but it seems probable that if a current of 10,000 exists side by side with one of 100, the use of sufficient iron wire of sufficient diameter would enable us to diminish the strength of the former considerably, while diminishing the latter to a much less degree.

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* Lord Rayleigh, Phil. Mag. vol. xxi. 1886, p. 387.

I employed a length of iron wire which had a resistance equal to 1·845 ohms, $l=4675$ centim.; taking $\mu=100$, we get when $p=2\pi\times 10{,}000$:—

$$\frac{p^2 l^2 \mu^2}{R^2} = 250 \text{ approx.}$$

The wire was placed between the secondary of the induction-coil (which had, as arranged, a resistance of about 24 ohms) and the Wheatstone bridge.

No very appreciable change was produced in the intensity of the sound of the telephone when the iron wire was introduced, nor was any change produced in the reading which gave the position of minimum sound.

The use of the telephone, as being too comprehensive in its record, seemed to me in some respects unsatisfactory; and I thought that possibly a method might be useful which enabled the telephone to be replaced by a galvanometer, whilst still retaining an alternating current.

It has already been mentioned that the interruptions were produced by means of a vibrating wire, a platinum point attached to the wire dipped in and out of mercury; to the same vibrating wire was attached, by means of an insulator, some platinum wire in the form of an inverted U, the lower tips of which just dipped in some mercury contained in two little vessels. The telephone was replaced by a galvanometer, and the latter was so connected to the bridge that the galvanometer-branch was only complete when the platinum wire (in the form of an inverted U) dipped into the mercury in the two little vessels.

This arrangement, as was to be expected, gave correct results when the resistance of a german-silver wire, for example, was determined by means of an alternating current; but when the attempt was made to determine the resistance of a bismuth spiral in a strong magnetic field, the method failed. Matters were sufficiently stable to allow of observations, but the results obtained varied with the frequencies, and even with the same frequency were not constant from hour to hour. Since readings could be obtained, and since $\frac{1}{10{,}000}$ of a second is no doubt small in comparison with the time the galvanometer-branch was complete, it seems extremely probable that the action of the bismuth spiral depends on some action upon the alternating current of the frequency I was endeavouring to employ (about 50). It seems likely also that the action of the bismuth is not a simple one, *i. e.* there is perhaps not merely (if at all) an increase in resistance, but also an action depending on the phase of the current.

It was thought probable that, although the bismuth spiral had no real self-induction, yet it might have something equivalent. To test this, two equal resistances were prepared whose coefficients of self-induction could be varied at pleasure, for description of which see Addendum III.

By no means could complete silence be obtained when the telephone and alternating current were employed; there was always a decided minimum noise. The minimum noise given by the telephone was certainly diminished by the introduction of suitable self-induction, the amount required diminishing with the strength of the field in which the bismuth was placed. But here, again, on attempting to measure I found difficulties; for the amount required varied from time to time, depending certainly on the state of the telephone (proved by tampering with the diaphragm), and possibly on the state of the ears, or on small peculiarities of the current.

The resistance of the bismuth spiral was determined alone and in series with an ordinary resistance, the alternating current and telephone being of course employed; the results were the same in each case: if the bismuth had behaved as if it had self-induction, the results would have been different.

The bismuth spiral was replaced by an ordinary resistance, and self-induction was introduced until the apparent change of resistance, measured by the telephone, was equal to that produced by the action of a magnetic field of certain strength on the bismuth: the minimum noise was very much greater than that observed when the bismuth was employed.

Before making more experiments, I thought it advisable to make up some theory as a working hypothesis.

In the first place, it is very probable that the increase of resistance with a *constant* current, produced by a strong magnetic field, is caused by, or accompanied by, a molecular or crystalline rearrangement of the bismuth. Again, it is not unlikely that the passage of a current along the bismuth may cause or require an additional rearrangement; and it is possible that an arrangement which has a certain resistance for one strength of current may not have the same resistance for another strength. It is not suggested that different strengths of current may be subject to different resistances, but that the arrangement for one strength of current may produce—the previous arrangement still obtaining—a different resistance for another strength of current. The changes in resistance would in this case be of a complicated character; I worked on the above assumption, assisted by mathematics, without obtaining any serviceable results.

I made another attempt at a theory, which, with the help of sufficient hypotheses, gives results agreeing to some extent with the facts.

For simplicity, initially, the bismuth spiral will not be considered as forming part of a Wheatstone bridge.

It is very probable that when the bismuth wire is put in a magnetic field the ultimate particles, crystals or molecules, will become magnetized. The stronger the field the stronger will the magnetization be. If now an alternating current be sent along the wire, the magnetized particles will take up forced oscillations.

Let $e=e_1 \cos pt$ represent the E.M.F. acting at the extremity of a bismuth wire.

For simplicity, let us confine our attention to one particle of bismuth. Let $u=$ any displacement of the particle caused by the alternating current; then, approximately, the oscillation of the particle will be represented by

$$\ddot{u}+k\dot{u}+n^2u=\mathrm{E}\cos pt; \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k depends on friction and damping, and $n=\frac{2\pi}{\mathrm{T}}$, T being the time of oscillation of the particle. T will depend on the degree of magnetization of the particle, on the strength of the field, and on the ultimate structure of the bismuth.

A solution of (1) is

$$u=\frac{\mathrm{E}\sin\epsilon}{pk}\cos(pt-\epsilon), \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where

$$\tan\epsilon=\frac{pk}{n^2-p^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Let $\epsilon=\frac{\pi}{2}-\alpha$; then from (3),

$$\tan\alpha=\frac{n^2-p^2}{pk}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Equation (2) may now be written

$$u=\frac{\mathrm{E}\cos\alpha}{pk}\sin(pt+\alpha). \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The movement of the particle will cause an E.M.F. along the wire; if the amplitude of the oscillation be small, the E.M.F. produced will vary approximately as $\frac{du}{dt}$.

From (5),

$$\frac{du}{dt}=\frac{\mathrm{E}\cos\alpha}{pk}.p\cos(pt+\alpha).$$

The p's cancel—this is an important part of the analysis—and we get

$$\frac{du}{dt}=\frac{\mathrm{E}\cos\alpha}{k}\cos(pt+\alpha). \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

If we assume that the value of pk is large in comparison with that of n^2-p^2, α will be small, and $\cos\alpha$ will approximately equal unity.

Let us suppose that $n>p$, so that α is positive.

Let e_b = the back E.M.F., due to the forced oscillation of the particle.

Let K = a multiplier which will increase with the magnetization of the particle, *i. e.* with the strength of the field.

We have

$$e_b=\mathrm{K}\frac{\mathrm{E}\cos\alpha}{k}\cos(pt+\alpha). \quad . \quad . \quad . \quad . \qquad (7)$$

Let i = current along the bismuth,
r = true resistance of the bismuth;

$$i=\left\{e_1\cos pt-\frac{\mathrm{KE}\cos\alpha}{k}\cos(pt+\alpha)\right\}\Big/r.$$

To obtain a rough result we may put $\alpha=0$,

$$i=\left\{\left(e_1-\frac{\mathrm{KE}}{k}\right)\cos pt\right\}\Big/r.$$

Let r_a = apparent resistance,

$$r_a=r\left(1+\frac{\mathrm{KE}}{ke_1}\right)\text{ approx.}$$

Let F = strength of magnetic field: for the sake of mathematical simplicity let us suppose that the magnetization of the bismuth particle varies as the square root of F.

We have

$$\mathrm{K}\propto\sqrt{\mathrm{F}},$$

$$\mathrm{E}\propto e_1\sqrt{\mathrm{F}}.$$

Let q = a multiplier; we obtain

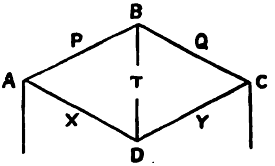
$$. \quad . \quad . \quad . \quad . \quad . \quad r_a=r(1+q\mathrm{F}). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

This deduction diverges from the observed facts; its chief interest lies in the result that, so long as k is great compared with $\frac{n^2-p^2}{p}$, the frequency of the alternating current has little influence. The higher the value of k, the lower is the frequency for which (8) is still true.

In the preceding it has been assumed that $n > p$; it seems impossible to obtain the actual value of n. In general, rapid oscillations are characteristic of small dimensions; and if the oscillations were due to mechanical causes, as an hypothesis I should feel inclined to take n large. The frequency of the oscillations of a magnetized particle could not depend entirely, however, on mechanical forces, for it would certainly depend on the strength of the field and the relative position of the particle with respect to the field.

It may be noticed also that r_a depends to some extent on p; and it will be shown later that, if the bismuth spiral formed one arm of a Wheatstone bridge, the positions of minimum noise would vary slightly with different frequencies; so that unless a perfectly harmonic alternating current was employed, the sound in the neighbourhood of the minimum position would differ in constitution from the sound corresponding to the original alternating current.

The preceding treatment is very incomplete, a fuller examination is given below.



The adjoining figure represents a Wheatstone bridge. The telephone is placed in BD, the bismuth spiral in CD. It will be assumed that the increase in resistance of the bismuth, when measured with a telephone, is altogether apparent.

Let Y = true resistance of the bismuth spiral.

Let X = Y, for simplicity.

Let $\frac{P}{P+Q} = b$, $\frac{Q}{P+Q} = a$.

Let us suppose the resistance of BD is so great that an inappreciable current goes through the telephone.

Let E.M.F. at A = 0.

„ „ $C = \mathfrak{E} \cos pt$.

Let i = current along C D A.

Let u = displacement of a bismuth particle,

$$\frac{d^2u}{dt^2} + k_1 \frac{du}{dt} + n^2 u = k_2 i. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Let B = back E.M.F. due to motion of bismuth particles; since the back E.M.F. will increase with the number of particles, if we confine our attention to the same kind of wire, we may put

$$B=k_3\frac{du}{dt}Y,$$

$$i=\frac{\mathfrak{E}\cos pt-B}{X+Y}=\frac{\mathfrak{E}\cos pt-k_3Y\frac{du}{dt}}{X+Y}. \quad . \quad . \quad . \quad (2)$$

Substituting in (1) and rearranging,

$$\frac{d^2u}{dt^2}+\left(k_1+\frac{k_2k_3Y}{X+Y}\right)\frac{du}{dt}+n^2u=\frac{k_2\mathfrak{E}\cos pt}{X+Y}.$$

Let

$$k_1+\frac{k_2k_3Y}{X+Y}=k, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\frac{k_2\mathfrak{E}}{X+Y}=E. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

We have

$$\frac{d^2u}{dt^2}+k\frac{du}{dt}+n^2u=E\cos pt;$$

the solution of which is

$$u=\frac{E\sin\epsilon}{pk}\cos(pt-\epsilon), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where

$$\tan\epsilon=\frac{pk}{n^2-p^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Supposing, as before, that k is great in comparison with $\frac{n^2-p^2}{p}$, ϵ will nearly equal $\frac{\pi}{2}$.

Differentiating (5),

$$\frac{du}{dt}=-\frac{E\sin\epsilon}{k}\sin(pt-\epsilon), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Substituting in (2),

$$i=\frac{\mathfrak{E}\cos pt+\frac{k_3YE\sin\epsilon}{k}\sin(pt-\epsilon)}{X+Y}.$$

E.M.F. at $D=iX$

$$=\frac{X}{X+Y}\left\{\mathfrak{E}\cos pt+\frac{k_3YE\sin\epsilon}{k}\sin(pt-\epsilon)\right\}$$

$$=\tfrac{1}{2}\left\{\mathfrak{E}\cos pt+\frac{k_3YE\sin\epsilon\cos\epsilon}{k}\sin pt-\frac{k_3YE\sin^2\epsilon}{k}\cos pt\right\}.$$

E.M.F. at $B=b\mathfrak{E}\cos pt$.

The current along BD varies as

$$\tfrac{1}{2}\left\{\mathfrak{E}\cos pt+\frac{k_3\mathrm{YE}\sin\epsilon\cos\epsilon}{k}\sin pt-\frac{k_3\mathrm{YE}\sin^2\epsilon}{k}\cos pt\right\}-b\mathfrak{E}\cos pt$$

or

$$\cos pt\left\{\frac{\mathfrak{E}}{2}-\frac{k_3\mathrm{YE}\sin^2\epsilon}{2k}-b\mathfrak{E}\right\}+\frac{k_3\mathrm{YE}\sin\epsilon\cos\epsilon}{2k}\sin pt$$

$$=\mathrm{R}\cos(pt-\alpha)\text{ say};$$

where

$$\mathrm{R}^2=\left\{\frac{\mathfrak{E}}{2}-\frac{k_3\mathrm{YE}\sin^2\epsilon}{2k}-b\mathfrak{E}\right\}^2+\left\{\frac{k_3\mathrm{YE}\sin\epsilon\cos\epsilon}{2k}\right\}^2$$

To make R a minimum,

$$b=\tfrac{1}{2}-\frac{k_3\mathrm{YE}\sin^2\epsilon}{2k\mathfrak{E}}.$$

From (4),

$$\frac{\mathrm{E}}{\mathfrak{E}}=\frac{k_2}{\mathrm{X}+\mathrm{Y}},$$

substituting

$$b=\tfrac{1}{2}-\frac{k_2k_3\sin^2\epsilon}{4k},$$

$$a=\tfrac{1}{2}+\tfrac{1}{4}\frac{k_2k_3\sin^2\epsilon}{k}$$

$$\text{Apparent resistance}=\frac{1+\tfrac{1}{2}\dfrac{k_2k_3}{k}\sin^2\epsilon}{1-\tfrac{1}{2}\dfrac{k_2k_3}{k}\sin^2\epsilon}.\mathrm{X}\quad.\quad.\quad.\quad(8)$$

If ϵ is nearly equal to $\frac{\pi}{2}$ the result is very little influenced by the frequency.

If $\epsilon=\frac{\pi}{2}$ we have, noticing from (3) that

$$k=k_1+\tfrac{1}{2}k_2k_3,$$

$$\text{Apparent resistance}=\frac{1+\dfrac{k_2k_3}{2k_1+k_2k_3}}{1-\dfrac{k_2k_3}{2k_1+k_2k_3}}.\mathrm{X}\quad.\quad.\quad.\quad(9)$$

It has been already mentioned that experiments in which a galvanometer and an intermittent contact caused by a vibrating wire were employed gave results of little utility. An objection to the method is that the length of contact and the position of contact (so to speak) with regard to the phase of the alternating current are unknown.

A well-designed alternator would provide a method of obtaining an alternating current almost perfectly harmonic in character, and by means of an intermittent contact arranged by the agency of the axis of the rotating armature the effect of the bismuth on the alternating current could be studied very efficiently.

I employed a small alternator made from a motor, the character of whose alternating current I do not know.

To make the tabulated results given later more clear, it may be mentioned that the wire of the bridge is divided into 1000 parts, and that increase in the reading means increase in the resistance measured.

The alternator gave a current with a frequency of about 30 or 40 per second.

With constant current and permanent contact, the reading was 489.

The reading for minimum noise with the telephone was about 501.

The readings obtained with an intermittent contact and a galvanometer are indicated in the table given below. I was assisted by a friend, and they were taken rapidly.

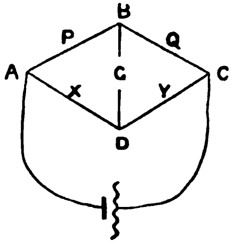
What is called the lead is the angle between the point of intermittent contact and the point of zero current: in other words, it is the angular distance the coil of the alternator has advanced beyond the position in which no current is produced before the galvanometer branch is made complete.

Lead. °	Reading of Bridge which gave no Deflexion of Needle of Galvanometer.
−5 roughly	405 approx.
0 ”	485 ”
10 ”	487 ”
30 ”	489 ”
90 ”	489 ”
135 ”	492 ”
175 ”	475 ”
180 ”	482 ”
225 ”	489 ”
270 ”	489·3 ”
315 ”	493 ”
362 ”	477 ”

It may be of interest to examine, by means of an example, what sort of results one would expect from reasoning on the principles explained above.

Let the E.M.F. acting at the extremities of the Wheatstone bridge be represented by $\mathfrak{E}\sin pt$, and the back E.M.F. acting in the bismuth spiral by $\frac{1}{30}\mathfrak{E}\sin(pt-45^\circ)$.

The adjoining figure represents a Wheatstone bridge.



The bismuth spiral is supposed to be in the arm CD.

CBA represents the bridge-wire divided into 1000 parts, the divisions counting from C to A.

Let X=Y ; this involves the assumption that the change in resistance of the bismuth is only apparent.

$$\text{Let } \frac{Q}{P+Q}=r, \quad \text{then } \frac{P}{P+Q}=1-r.$$

The theoretical change in resistance of the bismuth spiral as determined by the telephone will first be calculated. Assuming that the current in BD is negligible, the current through the telephone varies as

$$\frac{X}{X+Y}\left\{\mathfrak{E}\sin pt-\frac{\mathfrak{E}}{30}\sin(pt-45^\circ)\right\}-\frac{P}{P+Q}\mathfrak{E}\sin pt,$$

or as

$$\frac{1}{2}\sin pt-\frac{1}{60}\sin(pt-45^\circ)-(1-r)\sin pt$$

$$=\sin pt\left(r-\frac{1}{2}-\frac{1}{60\sqrt{2}}\right)+\cos pt\left(\frac{1}{60\sqrt{2}}\right)$$

$$=R\sin(pt-\alpha) \text{ say.}$$

Where

$$R^2=\left(r-\frac{1}{2}-\frac{1}{60\sqrt{2}}\right)^2+\left(\frac{1}{60\sqrt{2}}\right)^2,$$

to make R^2 a minimum we have

$$r=\frac{1}{2}+\frac{\sqrt{2}}{120}=\cdot5118 \text{ approx.}$$

Reading = 511·8 approx.

$$\frac{\text{Resistance with telephone}}{\text{Resistance with steady current}}=\frac{511{\cdot}8}{488{\cdot}2}=1{\cdot}048.$$

In the case of intermittent contact no current will go through the galvanometer when

$$(1-r)\sin pt=\frac{1}{2}\left\{\sin pt-\frac{1}{30}\sin\left(pt-\frac{\pi}{4}\right)\right\},$$

$$(1-r)=\frac{1}{2}\left\{1-\frac{1}{30}\frac{\sin(pt-45^\circ)}{\sin pt}\right\}.$$

Let $pt=+\delta\theta$, when $\delta\theta$ is infinitesimally small $r=-\infty$,
„ $=-\delta\theta$, „ „ „ „ $r=+\infty$;
nothing corresponding to these results can be obtained in practice.

In the above equation the contact is supposed to be of infinitesimal duration; as a matter of fact this is not the case: let $\tau=$ time of contact, then a more correct equation would be

$$(1-r)=\frac{1}{2}\left\{1-\frac{1}{30}\frac{\int_t^{t+\tau}\sin(pt-45^\circ)\,dt}{\int_t^{t+\tau}\sin pt\,dt}\right\}.$$

However, this equation, integrated, would also give rise to expectations of discontinuity in r, when

$$t=-\frac{\tau}{2},\quad \pi-\frac{\tau}{2},\quad 2\pi-\frac{\tau}{2},\ \&c.$$

It will be interesting to find what would be the theoretical readings for various values of pt.

I. Let $pt=30^\circ$,

$$(1-r)=\frac{1}{2}\left\{1+\frac{1}{30}\frac{\sin 15^\circ}{\sin 30^\circ}\right\}=\cdot 5086.$$

$r=\cdot 4914$; Reading $=491$.

II. Let $pt=60^\circ$,
$(1-r)=\cdot 495$, $r=\cdot 505$. Reading $=505$ approx.

III. Let $pt=90^\circ$,
$(1-r)=\cdot 4882$, $r=\cdot 5118$. Reading $=512$ „

IV. Let $pt=120^\circ$,
$(1-r)=\cdot 4814$, $r=\cdot 5186$. Reading $=519$ „

V. Let $pt=150^\circ$,
$(1-r)=\cdot 4678$, $r=\cdot 5322$. Reading $=532$ „

VI. Let $pt=180^\circ$,
r changes from $+\infty$ to $-\infty$.

VII. Let $pt=210^\circ$. Reading $=491$.
VIII. Let $pt=240^\circ$. Reading $=505$.
IX. Let $pt=270^\circ$. Reading $=512$.
X. Let $pt=310^\circ$. Reading $=519$.
XI. Let $pt=330^\circ$. Reading $=532$.

The theoretical results indicate a sudden change at 0°, involving an impossibility of reading for small values of pt (r must lie between $+1$ and 0); later a gradual rise in reading to 180°, again a sudden change, and a repetition of the preceding.

The measurements of the angles of lead are confessedly rough (they were made with the unassisted eye), theory would indicate an addition of 5° to each reading. I endeavoured to make more observations, but owing to difficulties decided to leave more accurate determinations to a future time.

Theory indicates that difficulties might be expected at the position with which I always started, viz., a lead of about zero.

I may mention that the telephones I employed were not nearly so useful with currents of low frequency as with higher. In fact a current from the alternator, which was none too powerful for use with the telephones and bridge, heated the bismuth spiral so as to perceptibly alter its resistance. I found that in a strong field the resistance of bismuth, as measured by a telephone, diminishes with increase of temperature: the same is true with a constant current, as, I found out after making my own experiments in May, was noticed by Van Aubel[*] a year or more ago, and later (with more detail) by Henderson[†].

That the resistance of bismuth in a strong field should diminish with increase in temperature is what one would expect if, as surmised, the increase of resistance is due to changes connected with the diamagnetism of bismuth. I do not know of any researches, but it is probable that the susceptibility of bismuth will diminish (numerically) with increase of temperature: assuming this, we should expect that the effect of an increase in temperature will be complex in character—that, so far as the effect of the demagnetization due to rise in temperature is concerned, the resistance will diminish; that, so far as the ordinary action of heat is concerned, the resistance will increase. In general we might expect a temperature to be soon reached at which the latter action is greater than the former.

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[*] *Journal de Physique*, September 1893, p. 108.
[†] Phil. Mag. November 1894.

I should expect the curves which give the relation between temperature and resistance, in the case of a steady current, to be somewhat (to express myself loosely) asymptotic, the asymptote being the line which gives the relation between the temperature and resistance when the bismuth is in zero field.

In addition, taking my theory—which may be applied to currents of the frequencies under consideration or to those of 10,000 per second as imagined, perhaps correctly, by Lenard—as a working hypothesis, I have formed the expectation that the difference between the resistances as measured by telephone and galvanometer would diminish with increase of temperature; this is perhaps worthy of investigation.

There is another action which may exist,—perhaps also worthy of research; I have not had the advantage of studying the original paper, but Geronza and Finzi * find that an alternating current influences the susceptibility of iron, nickel, and steel; possibly the susceptibility of bismuth may be influenced in like manner, and indirectly affect the resistance.

I hope at some future time to carry on some experiments with alternating currents perfectly harmonic in character, a telephone responding only to the frequency under consideration, and to endeavour to determine what is the lowest frequency at which a change in resistance is perceptible; also to examine whether the shape of the section of the bismuth wire is of any importance.

Summary.

The paper contains a few new experiments dealing with the action of alternating currents when sent through the coils of a galvanometer.

A convenient and satisfactory arrangement is described for diminishing the spark on breaking a galvanic circuit.

A description is given of experiments, made with the bismuth spiral, all of which (and others of which no description is given) gave negative results.

A theory is elaborated which explains, to a limited extent, the fact that in a strong field the resistance of bismuth is greater when measured with an alternating than with a constant current.

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* *Beiblätter*, vol. xviii. No. 3, p. 375.

There are some surmises with regard to the action of a rise of temperature.

Addendum I. contains a thorough discussion of the behaviour of the method of differential winding for diminishing the spark on breaking a galvanic circuit.

Addendum II. gives a theoretical treatment of the working of the interrupter which may be useful when it is necessary to design an interrupter for high frequencies.

Addendum III. describes the method adopted to compare self-inductions.

In conclusion I have to express my thanks to Prof. A. Schuster for initiating my research and for much friendly criticism throughout.

ADDENDUM I.

In the method of differential winding two wires of equal length and diameter are wound into coils side by side, and their ends so connected that the wires are in parallel arc and that the equal currents which circulate the coils, when a steady current is flowing, go in opposite directions. When a steady current goes through the arrangement *no lines of force* are produced within the combination coil; one naturally associates the production of a spark at a break in a coil with lines of force, and there is a danger of erroneously assuming that no spark due to induction will be formed by causing a break in one of the coils. What is, of course, necessary, is that the rate of change of the number of lines of force enclosed within the coil should equal zero.

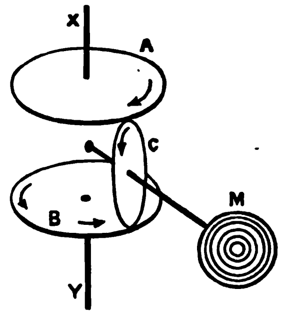
Let us imagine that one coil can be suddenly broken at any point, and that the current in the other coil can flow on undisturbed: if this happened the lines of force enclosed within the combination coil would instantaneously vary from zero to a finite number, *i.e.*, the rate of change of the number of lines of force would equal infinity and the E.M.F. tending to produce a spark across the gap would also equal infinity.

What actually happens is, probably, somewhat as follows: since the self-induction of each coil is equal to the mutual induction of the two, on breaking one coil the current in the other is suddenly stopped, it then begins immediately to increase, and whilst increasing causes, by induction, a spark across the gap in the broken coil.

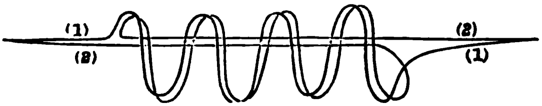
The spark produced by the break is therefore analogous to the "make" spark of an ordinary induction-coil.

The stoppage of both currents by the break of only one coil is capable of explanation by means of a mechanical analogy.

In the figure, A represents a disk capable of rotation about a vertical axis; M a heavy body which is capable of rotation about a vertical axis X Y; C a disk capable of rotation about an axis (variable in position) joining M to X Y; B a disk similar to A. The disks A, B, and C are supposed to be of inappreciable mass. If A and B (corresponding to currents) rotate with equal velocities in opposite directions, the disk C will rotate, but M (corresponding to induction) will remain stationary. If, now, B be suddenly stopped, as M, owing to its inertia, must instantaneously remain at rest, C will be instantaneously stopped also, and likewise A. If the motive power of A be kept continuously applied, it will immediately begin to rotate, and gradually increase in velocity from zero to its maximum speed.



The cause of the production of the spark is also capable of mathematical treatment.



For simplicity, let it be assumed that the E.M.F. between the ends of each coil is kept constant and equal to E.

Let i_1 be the current in coil (1).
i_2 „ „ (2).
L = coefficient of self-induction of each coil.
M = coefficient of mutual induction.

Considering coil (1),

$$E = i_1 r_1 + L\frac{di_1}{dt} - M\frac{di_2}{dt}. \quad \ldots \ldots \quad (1)$$

Considering coil (2),

$$E = i_2 r_2 + L\frac{di_2}{dt} - M\frac{di_1}{dt}. \quad \ldots \ldots \quad (2)$$

Since L=M, equations (1) and (2) may be written

$$E = i_1 r_1 + L\frac{di_1}{dt} - L\frac{di_2}{dt}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$E = i_2 r_2 + L\frac{di_2}{dt} - L\frac{di_1}{dt}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The problem is to find how i_2 varies if a break is made in coil (1), *i. e.* if r_1 varies from a finite to a great or infinite value.

Adding corresponding sides of (3) and (4),

$$2E = i_1 r_1 + i_2 r_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Differentiating,

$$0 = i_1\frac{dr_1}{dt} + r_1\frac{di_1}{dt} + r_2\frac{di_2}{dt}. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

From (5),

$$i_1 = \frac{2E - i_2 r_2}{r_1}.$$

From (4),

$$\frac{di_1}{dt} = \frac{i_2 r_2 + L\frac{di_2}{dt} - E}{L}.$$

Substituting these values in (6),

$$0 = L(2E - i_2 r_2)\frac{dr_1}{dt} + r_1^2 r_2 i_2 + L r_1^2\frac{di_2}{dt} - r_1^2 E + L r_1 r_2\frac{di_2}{dt}.$$

The last equation would probably, under any assumption, produce an intractable differential equation. However, the difficulty can be avoided by not troubling about r_1 for the present, and assuming that i_1 varies from a finite value to zero; later it will be proved that the assumption is consistent with the conditions of the problem, *e. g.* that the expression deduced for r_1 is quite a legitimate one.

Let

$$i_1 = i_0 e^{-\kappa t};$$

then

$$\frac{di}{dt} = -\kappa i_0 e^{-\kappa t};$$

and on substituting (4) becomes

$$E = i_2 r_2 + L\frac{di_2}{dt} + \kappa L i_0 e^{-\kappa t}.$$

A solution is

$$i_2 = \frac{E}{r_2} - \frac{\kappa i_0 L}{r_2 - \kappa L}e^{-\kappa t} + Ce^{-\frac{r_2}{L}t}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

When $t=0$, $i_2=i_0$, substituting and manipulating,

$$C=\frac{\kappa i_0 L}{r_2-\kappa L}.$$

Finally (7) becomes

$$i_2=i_0-\frac{\kappa i_0 L}{r_2-\kappa L}e^{-\kappa t}+\frac{\kappa i_0 L}{r_2-\kappa L}e^{-\frac{r_2 t}{L}}. \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

It will now be necessary to prove that r_1 is a possible function of t. It is needless to give the details, but it can readily be shown that

$$r_1=\frac{\kappa L r_2}{r_2-\kappa L}+\frac{E}{i_0}e^{\kappa t}+\frac{\kappa L r_2}{\kappa L-r_2}e^{\left(-\frac{r_2}{L}\right)t}. \quad . \quad . \quad . \qquad (9)$$

Let $k>\frac{r_2}{L}$, then an examination of (9) shows that r_1 is initially equal to $\frac{E}{i_0}$ and continually increases with t.

We may now, with safety, study the nature of the solution

$$i_2=i_0-\frac{\kappa i_0 L}{r_2-\kappa L}e^{-\kappa t}+\frac{\kappa i_0 L}{r_2-\kappa L}e^{\frac{-r_2 t}{L}};$$

differentiating,

$$\frac{di_2}{dt}=\frac{\kappa^2 i_0 L}{r_2-\kappa L}e^{-\kappa t}-\frac{r_2 \kappa i_0 L}{L(r_2-\kappa L)}e^{-\frac{r_2}{L}t}.$$

When $t=0$,

$$\frac{di_2}{dt}=\frac{\kappa^2 i_0 L}{r_2-\kappa L}-\frac{\kappa i_0 r_2}{r_2-\kappa L},$$

the value of this when κ is very great is approximately

$$-\kappa i_0+\frac{i_0 r_2}{L}.$$

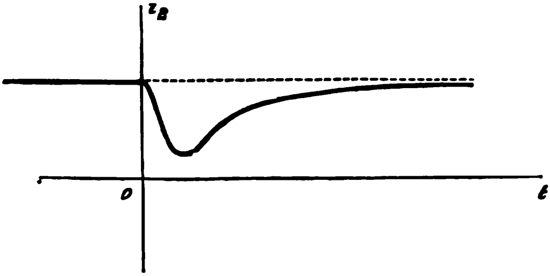
This result shows that if κ is very great, i_2 initially diminishes very rapidly.

It is useless to give the details, but it can be shown that the minimum value of i_2 is

$$i_0-\frac{\kappa i_0 L}{r_2-\kappa L}e^{\frac{-\kappa L}{\kappa L-r_2}\log\left(\frac{\kappa L}{r_2}\right)}+\frac{\kappa i_0 L}{r_2-\kappa L}e^{\frac{-r_2}{\kappa L-r_2}\log\left(\frac{\kappa L}{r_2}\right)}.$$

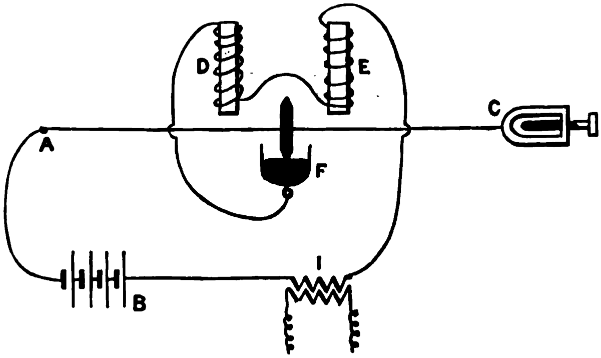
If $\kappa=\infty$, the above becomes an indeterminate expression the limiting value of which is zero, showing that if the coil (1) is completely and rapidly broken, the current in coil (2) is, under the given conditions, instantaneously diminished to zero.

The probable relation between i_2 and t when κ is great, but not infinite, is indicated in the figure below.



ADDENDUM II.

The apparatus used as an interrupter is diagrammatically sketched below.



A C represents the vibrating wire, B the battery, D and E electromagnets, F a vessel containing mercury, I the induction-coil. Some cells, consisting of lead plates in dilute sulphuric acid, were used as a shunt across the spark-gap; they are not shown in the figure, nor are they taken account of in the theoretical considerations which are given below.

It was found experimentally, as one would expect from telephony, that initial magnetization by means of subsidiary coils increased the amplitude of vibration, at any rate for low frequencies.

It was also found that a piece of iron placed below one of the electromagnets increased the amplitude; this is a corresponding device to that used in Auer's telephone. The probable explanation is that the iron produces a strong and divergent field in the neighbourhood of the iron wire.

If there is a strong initial magnetization, we may assume that the efficient pull on the wire will vary as the current through the coils.

Let F = efficient pull,

i = current,

then $F \propto i$.

Some rough calculations were made, and the conclusion was arrived at that the self-induction of the electromagnets was of the dimensions of 10^9 in C.G.S. units.

The resistance of the primary circuit was about 3×10^9 C.G.S. units.

Let T = time of vibration,

$n = \text{frequency} = \frac{1}{T}$,

let i_f = maximum current in the primary circuit, *i. e.* the current just before the break.

Let it be assumed that the platinum point is in contact with the mercury for the time $\frac{T}{2}$.

Let $i_0 = \frac{E}{R}$, where E equals the E.M.F. and R the resistance of the primary circuit.

The equation which represents the rise in the current after contact is made is

$$i = i_0 (1 - e^{\frac{-Rt}{L}}). \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

When t is small,

$$i = i_0 \frac{Rt}{L}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Calculations showed that if $T = 2$, $i_f = i_0 \times \cdot 94667$; $T = \frac{1}{5}$, $i_f = i_0 \times \cdot 2541$; $T = \frac{1}{50}$, $i_f = i_0 \times \cdot 03$; $T = \frac{1}{500}$, $i_f = i_0 \times \cdot 003$; $T = \frac{1}{1000}$, $i_f = i_0 \times \cdot 0015$; and that if $n > 50$, formula (2) may, with very little error, be taken as correct. It can be shown that the average current in the primary circuit varies inversely as the frequency.

The energy given to the vibrating wire in one complete oscillation will now be considered.

Since the current is stronger whilst the wire is rising than when descending, the work done *on* the string by magnetic forces when rising must be greater than the work done *by* the string against magnetic forces when descending; the spark will also prolong the pull upwards.

In the following the effect of the spark will be entirely omitted.

As a matter of fact, the oscillation of the wire cannot be perfectly harmonic; nevertheless, let us assume that the motion of the wire is represented by the equation

$$x = d \sin pt,$$

where $d =$ maximum distance traversed from the middle point,

$p = \frac{2\pi}{T}$,

$x =$ distance of platinum point below its middle position.

The work done by the electromagnets on the wire can be put in the form $\int F dx$, taken between the proper limits where F varies as i, i. e. $F = kt$, where k varies as $\frac{i_0 R}{L}$.

It is needless to go into details, but the result is that the resultant work done on the string in one oscillation

$$\text{varies as } \frac{i_0 RTd}{L},$$

$$i.\ e. \qquad \text{as } \frac{ETd}{L};$$

which shows that the energy given to the wire in one oscillation varies inversely as the frequency if the amplitude is unaltered.

When the vibrating wire has settled down, the energy given to the wire in each oscillation by magnetic causes must equal the energy lost through other causes.

I. Air resistance, which may be taken to vary as the square of the velocity of the string.

II. Resistance due to induced currents or damping, which may be taken to vary as the velocity.

III. Other frictional losses, which will be neglected.

By equating the energy given to the energy lost, and dealing only with the losses under (I.), I obtain the result that

$$E \text{ varies as } n^3;$$

so that, as 4 cells were used to obtain a frequency of 500, to obtain a frequency of 1000 of the same amplitude 32 cells would be required.

If the chief losses come under (II.), then E varies as n^2.

In what follows, the losses under (I.) will alone be considered.

If n increases, the amplitude diminishes, the relation being that d varies as $n^{-\frac{3}{2}}$.

The wire ceases to vibrate if i_0 is not sufficiently great; it is hard to say what decides the cessation of vibration; if the platinum point acted perfectly, *i. e.* if the least rise broke the circuit completely, and the least depression made the circuit, there would, I think, be no limit to the frequency obtainable.

If we assume that it is necessary for the platinum point to move a certain minimum distance before a break is made in the circuit, then, for the wire to continue vibrating,

$$\text{E must vary as } n^2.$$

Theory indicates that the frequency obtainable by the apparatus discussed could be raised by increasing E and at the same time adding resistance free from induction.

The preceding discussion applies to the apparatus under consideration; but the subject can be treated more generally.

Let it still be assumed that F varies as i; so that we may put $\mathrm{F}=\mathrm{K}i$.

Let $x=a \sin pt$,

where x = distance of platinum point below its middle position,
a = maximum deflexion of vibrating wire.

$$p=\frac{2\pi}{\mathrm{T}},$$

and T = time of vibration.

Let $i_0=\frac{\mathrm{E}}{\mathrm{R}}$, then

$$i=i_0(1-e^{\frac{-\mathrm{R}t}{\mathrm{L}}})dx.$$

The work done by the wire against magnetic forces whilst going downwards equals $\int \mathrm{F}dx$ or $\int \mathrm{K}idx$, taken between the proper limits; the work done on the wire whilst ascending also equals $\int \mathrm{K}i\,dx$, taken, of course, between other limits.

I omit the details, which are tedious, and give the final result, which is that if W equals the resultant work done on the wire in one vibration, then

$$\mathrm{W}=\frac{\mathrm{K}i_0pa\mathrm{RL}(1+e^{\frac{-\mathrm{RT}}{\mathrm{L}}})}{\mathrm{R}^2+\mathrm{L}^2p^2},$$

If T is small, it can be shown that this expression agrees with the previously obtained result.

In order to obtain the greatest amplitude for a particular frequency, W must be a maximum; its maximum value cannot easily be found—at any rate, by the ordinary treatment; without finding the particular value, however, it can be indicated that there is a certain value of L which produces the most efficient result.

If L=0, W equals 0; if L=∞, W equals zero; so that there is some value of L between 0 and ∞ which it is best to employ.

The actual problem, which I have not gone into, is more complicated still; for both K and L depend on the winding: for precise treatment, a certain type of winding might be adopted, and K and L made to depend on some variable depending on the character of the winding; perhaps experiments would give results more readily than mathematics.

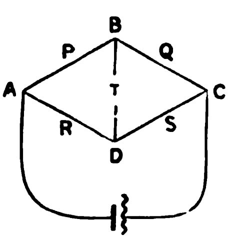
ADDENDUM III.

Each resistance of variable self-induction was made of two bobbins, one of which rotated within the other, after the manner of those described by Lord Rayleigh in Phil. Mag. 1886, xxii. p. 473.

To compare and graduate the self-inductions I used a method which was very convenient and sensitive, a modification of that described in Clerk-Maxwell, vol. ii. art. 757.

The adjoining figure represents a Wheatstone's bridge; the letters have their usual significance. Let self-induction of AD=L, of CD=L′.

P, Q, R, S were arranged so that with a steady current and galvanometer no current went through the galvanometer.



The galvanometer was then replaced by a telephone, the steady by an alternating current, and the rotating bobbin of one of the resistances was rotated until no noise was heard in the telephone. In this case

$$\frac{L}{L'}=\frac{R}{S}=\frac{P}{Q}.$$

XXIV. *On Electromagnetic Stress.* *By* E. TAYLOR JONES, *B.Sc., Science Scholar of Royal Commission for Exhibition of* 1851, *nominated by the University College of N. Wales*[*].

THE problem of finding experimentally the true relation between electromagnetic stress, or "lifting-power" per unit area of magnets, and magnetization has been attacked by many experimenters during the last sixty years; but no one has succeeded in determining accurately what function of the intensity of magnetization or of the induction the stress really is. In order to show how the methods of experimenting have developed, and how they have led to those of the present investigation, I will describe shortly the chief experiments that have so far been made[*].

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[*] Communicated by Lord Playfair, F.R.S.

As long ago as 1833 Fechner[†] made a series of measurements of the weight necessary to separate a horseshoe magnet and its keeper, measuring the current by swinging a magnetic needle within a coil through which the current passed. He found a rough proportionality between the limiting weight and the current.

Somewhat more accurate experiments made in 1839 by Lenz and Jacobi[‡] showed that this proportionality did not exist. In the same year Joule[§], measuring the magnetizing current with an ingenious "current-weigher," found that for small currents the lifting-power of an iron electromagnet was proportional to the square of the magnetizing current, but that for stronger currents the lifting-power increased more slowly and ultimately reached a maximum value of 140 lb. per square inch; twelve years later[‖], however, using a more powerful electromagnet, he found the maximum value to be 175 lb. per square inch.

In 1852 Dub[¶] found that the lifting-power was proportional neither to the current nor to the square of the current, but to some intermediate function, and for strong currents reached a maximum.

Much more accurate experiments were made in 1870 by v. Waltenhofen[**]. Two similar bars of iron with plane ends were bent approximately to semicircles and wire wound evenly on both. One bar was fixed rigidly in a frame and the other one pulled up from it, the necessary force being measured by a spring-balance. A third bar and coil, similar to the other two but straight, was set up with a compensating-coil in the East and West line through a magnetometer-needle. All these coils were in circuit with a galvanometer for indicating the current.

The stress between the bent electromagnets could thus be compared with the magnetic moment of the straight one, and with the magnetizing current. With small currents the lifting-power increased more rapidly than the magnetometer-deflexion, but with stronger currents more slowly, the corresponding curve ultimately approaching a horizontal asymptote. Also the lifting-power was proportional neither to the current nor to its square, but was represented approximately by a function of the form $b \tan^{-1} (ac)$, where c is the current, and a, b constants.

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[*] *Cf.* also Wiedemann, *Elek.* iii. Bd. 3, pp. 632–654; du Bois, *Magnetische Kreise*, sect. 105–110 (1894).

[†] Schweigg. *Journ.* lxix. (1833).

[‡] Pogg. *Ann.* xlvii. p. 415 (1839).

[§] Phil. Mag. Dec. 1851.

[‖] Ibid. Jan. 1852.

[¶] Pogg. *Ann.* lxxxvi. p. 553 (1852).

[**] *Wien. Ber.* lxi. p. 739 (1870).

The magnetizing forces, however, used in these experiments could have been but small, since the straight magnet was never more than half saturated, and its magnetization was always nearly proportional to the current.

The next experiments were made in 1881 by Werner v. Siemens[*]. The electromagnets were made by cutting an iron tube in a plane through the axis, and winding both halves with wire. The interfaces were carefully ground together. A ballistic galvanometer and secondary coil were used to measure the induction. From the total induction-"throw" was subtracted the throw caused by breaking the current in the coil after the iron was removed. The resulting differences are therefore proportional to the intensity of magnetization, not to the induction.

The result showed that the lifting-power was approximately proportional to the magnetic moment per unit volume, but that the ratio somewhat increased as the current was increased. Similar results were obtained with electromagnets formed by cutting a circular iron tube in the plane through the greatest section.

Siemens believed the above law to be established, and attributed the deviations to residual magnetism, and to imperfect contact of magnet and keeper due to bending, the imperfect state of the surfaces, and other mechanical causes. These were the probable causes of much greater errors than those believed to exist.

In 1882 Wassmuth[†] experimented with magnets similar to those used by v. Waltenhofen. The induction was measured ballistically, and the ends of the magnets were ground plane and polished. The magnetic moment per unit volume was calculated from the induction-current and the results compared with a theory given by Stefan[‡], according to which the stress is proportional to the square of the magnetic moment per unit volume at the surface of contact. Wassmuth found, however, that the stress agreed better with an expression of the form

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[*] Wied. *Ann.* xiv. p. 640 (1881).
[†] *Wien. Ber.* lxxxv. p. 327 (1882).
[‡] *Ibid.* lxxxi. ii. p. 89 (1880).

$$a+bI^2+\frac{cI^2}{d+cI^2},$$

where I is the magnetic moment per unit volume. Wassmuth's experiments are subject to the same objections as Siemens', viz., imperfect contact of magnet and keeper due to bending &c., and, in addition, to the difficulty of ensuring that the magnets separate at the two places of contact exactly simultaneously. If separation takes place at one place first, there will be an immediate diminution of the induction, and the limiting weights will generally be too small.

Wassmuth further deduced from Siemens' numbers an expression for the lifting-power of the form $a+bI^2+cI^4$, which represented the latter's results fairly well.

Neither Siemens nor Wassmuth appears to have thought of comparing his results with the theory given in sections 641–644 of Maxwell's 'Electricity and Magnetism,' which had been published several years before. Maxwell there arrives at the expression $B^2A/8\pi$ for the electromagnetic traction in air between two opposing, plane, infinitely near, and uniformly and normally magnetized pole-faces each of area A; where B is the induction.

In 1886 Bosanquet* experimented with two straight iron electromagnets whose ends were ground together. One electromagnet was fixed vertically, and the other supported beneath it on the beam of a balance by which its weight was compensated, this allowing measurements with very small currents to be made. Weights were placed in a scale-pan suspended from the lower electromagnet, and the induction was measured by a small secondary coil near the surface of contact.

For low and medium currents the weights supported were much greater than those given by Maxwell's theory, the values being better represented by an expression of the form $aB+bB^2$; while with high currents the results appear to be very uncertain, most of the readings widely differing from the theoretical values. The mean results, however, agree to within about 5 per cent.

In the same year Bidwell† made a series of measurements of the tractive force between two bar-magnets, and of the magnetizing current, but not of the induction, his object being to measure the induction from the values of the tractive force, using Maxwell's expression.

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* Phil. Mag. xxii. p. 535 (1886).

† Proc. Roy. Soc. xl. p. 486 (1886).

Quite recently an important paper has been published by Threlfall[*], giving an account of experiments made with apparatus essentially similar to Bosanquet's; but the interfaces of the electromagnets were carefully ground and polished, and the tractive force was measured by a spring-balance.

The results for high inductions do not show better agreement than Bosanquet's with Maxwell's theory; but the author explains an important source of error which exists especially in working at low inductions, viz.—that the interfaces of the magnets do not generally remain in contact until the stress is completely overcome, but separate at one side first, thus enclosing a "wedge-shaped gap." The numbers given, however, only extend over a range of inductions from 11,000 to 16,000 C.G.S. units. Most of the paper deals with the case when the bars are separated by layers of non-magnetic substance.

It was clear, therefore, that more accurate experiments were necessary to determine whether Maxwell's expression represents exactly the tractive force, and if so, how apparatus is to be arranged so as to allow of the accurate measurement of induction by tractive experiments.

Present Experiments. Apparatus.

The following experiments were begun in October 1893. The apparatus was devised with a view to realizing as closely as possible the conditions under which the results could best be compared with Maxwell's theory, and was prepared and arranged as follows:—

A chosen bar of soft German iron was turned accurately to an ellipsoid of revolution of length 22·57 centim. and least diameter 1·5 centim. Its shape was tested by measuring its volume by weighing in air and water, and by calculating the volume from the above values of the axes. The two values agreed to within a tenth per cent. The ellipsoid was afterwards cut through in the equatorial plane, the diminution of length being measured by observing the distance between two marks on its surface.

Two exactly similar magnetizing-coils were made, each 20 centim. long., and having 12 layers of 70 turns each of 2 millim. aluminium wire[†].

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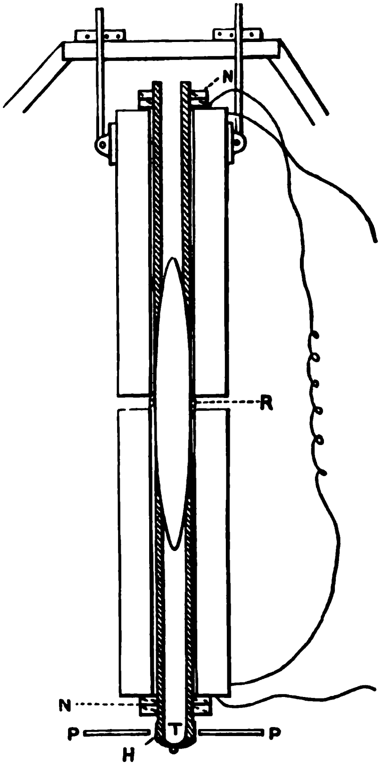
[*] Phil. Mag. July 1894.

[†] Aluminium wire was used that the coils might be as light as possible, it being thought desirable not to use the compensating arrangement adopted by Bosanquet, as this probably introduced errors due to friction.

The two halves of the ellipsoid were soldered into tubes which could be fitted tightly, axially, into the coils, the free ends projecting by amounts regulated by nuts, N (fig. 1), running on the tubes. To secure good alignment of the half-ellipsoids, a small brass ring, R, of 1 millim. width, was made to fit tightly on one half and loosely on the other at the plane of contact. This ring was afterwards found to be an important part of the apparatus, results obtained without it being very uncertain.

Fig. 1.—Longitudinal vertical section of Traction Apparatus.



To the absence of such a guide in Bosanquet's experiments may probably be attributed, to some extent, the uncertainty of his results, especially at high inductions.

One coil was suspended from a tripod stand by two rods provided with nuts and screws, by which and two other screws (not shown in the diagram) the coil could be raised or lowered, levelled, and rigidly fixed. Below this was a platform, P, with an opening through which passed the lower projecting end of the tube in the other coil, and to this was attached a hook and scale-pan.

The current, obtained from a battery of accumulators, was measured by a Siemens and Halske's torsion-galvanometer, standardized by electrolysis.

The magnetization was measured in independent experiments by the magnetometer method.

The ellipsoid and coils were placed in the magnetic east and west line east of a delicate magnetometer read by telescope and scale.

The intensity of the earth's horizontal field was measured by the method of Gauss and by the tangent-galvanometer method, a Kohlrausch's local-variometer being found useful for measuring its variations.

The *magnetization-curve* was first obtained, showing the relation between I and H, allowance being made, as usual, for the demagnetizing-force of the ellipsoid calculated from the expression given in Maxwell's 'Electricity and Magnetism' (Sect. 438). The intensity of magnetization I was calculated in absolute units from the formula*

$$h\tan\theta=\frac{2v\mathrm{I}}{d^3}\left\{1+\frac{6}{5}\frac{e^2}{n^2}+\frac{9}{7}\frac{e^4}{n^4}+\frac{4}{3}\frac{e^6}{n^6}+\dots\right\},$$

where h = earth's horizontal field, θ = deflexion of needle, v = volume and e = eccentricity of ellipsoid, d = distance of needle from centre of ellipsoid (the former being in the prolongation of the axis of the latter), and $n=\frac{d}{c}$, c being the semiaxis of the ellipsoid.

This curve being determined once for all, the induction B corresponding to any current could be calculated, since $\mathrm{B}=\mathrm{H}+4\pi\mathrm{I}$†. All precautions were taken to determine the curve as accurately as possible, the torsion of the magnetometer-fibre, the exact position of the needle with respect to the axis of the ellipsoid, the length of a division on the scale, the effect of the compensating-coil at all parts of the scale (by deflecting with permanent magnets), and the temperature of the room during the local-variometer experiments all being carefully examined. The residual magnetism was very small, being less than a sixtieth of the total magnetization when the ellipsoid was strongly magnetized. Each current was reversed, and half the double deflexion of the needle taken as the deflexion corresponding to the mean of the two currents, which were generally the same*.

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* This was obtained from Thomson and Tait's expression for the potential at an external point due to an ellipsoid of attracting matter by differentiating twice with respect to the distance of the point. (*Cf.* Roessler, *Dissertation*, Zürich, 1892).

† Where H = Field due to coils − demagnetizing force of ellipsoid.

The "*lifting*" *experiments* were then proceeded with:—

The upper coil was first suspended vertically and symmetrically above the opening H, in the platform P (fig. 1), the lower bar and coil being thus supported (when the current was made) so that its tube T passed freely through the opening H.

Enough weights were placed in the scale-pan to nearly overcome the stress, the remainder being slowly poured in in the form of fine shot until the lower coil fell. The current was then read off and the shot weighed.

This was repeated for a number of currents ranging from 1 to 10 amperes (the corresponding inductions ranging from 6000 to 20,000 C.G.S.); the adjustment of the upper coil being made before every reading, and the surfaces carefully cleaned with a soft dry brush.

The "reversed" readings were also taken, as in the magnetometer experiments.

The inductions corresponding to the currents used were calculated from the magnetization-curve. The inductions and the square roots of the observed weights were plotted in a diagram along with the straight line representing Maxwell's law.

First Experiments.

The first experiments were made with the contact-surfaces of the ellipsoid turned truly plane but not polished.

The curve representing the observed results was at low inductions considerably above the straight line (the observed weights being greater than those given by Maxwell's law), soon crossing it and remaining below it for high inductions, the difference increasing with the induction.

The correction due to the excess of area of the coils over that of the core was found by removing the cores and supporting the lower coil in the same position on a balance.

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* (1) It may be objected that the magnetization in the "lifting" experiments was not the same as in the magnetometric experiments, on account of the longitudinal pull existing in the former; but a small calculation shows that, with the weights used, this effect was in general very small, and could, except perhaps at the highest inductions, be neglected.

(2) The magnetization-curve was determined both before and after the ellipsoid was cut, and the demagnetizing-force (which was affected by the shortening of the ellipsoid after the cutting) calculated in both cases. The curve for the cut ellipsoid was lower than the other; but the difference was very slight, especially at high fields.

The current was made, and weights added until the coil returned to its original position. These added weights measured the total attraction of the coils. From this must be subtracted the part corresponding to the area occupied by the core, since this is already included in B.

The correction was found to be negligible, never being more than a sixth per cent. of the attraction of the electromagnets, and for small currents less than a twentieth per cent.

Another correction is due to the effect of the surface-distribution of magnetism on the ellipsoid in so far as the corresponding tubes of force pass through the air. This correction, which vanishes with ring-magnets and infinitely long cylinders, was found on calculation to amount to less than $\frac{1}{10}$ per cent.

The interfaces of the ellipsoid were then polished by the firm Hartmann and Braun of Frankfurt. In this process the surfaces were surrounded with wide "guard-rings" to keep the edges as sharp as possible. The mirrors showed a so-called "black polish," and gave a perfectly clear image with a 32-magnifying-power telescope and scale at a distance of 5 metres. It would be hardly possible to obtain on metal a nearer approach to an absolutely geometrical plane.

Also in order better to guide the lower coil, the opening in the platform P (fig. 1) was made smaller, just large enough, in fact, to allow the tube to pass freely through it. A series of readings was taken, as before, and these agreed considerably better with Maxwell's theory both for low and for high, but especially for low inductions.

This I attributed chiefly to the improved guiding of the lower coil; and it was found that at low inductions, by very slightly altering the position of the upper coil, a position could be found in which the tractive force was a minimum, and that if the applied weights were rather less than this minimum value the upper coil (never being *absolutely* rigidly fixed), on being slowly moved towards the "minimum" position, suddenly jumped across it, thus showing, so to speak, a preference for positions in which it could support heavier weights or the actual weight more easily.

The measurements were therefore made as follows:—The current being kept constant, shot was poured into the scale-pan in small instalments, the upper coil after each addition being carefully moved by hand until the "minimum" position (easily observed by the jerk) was found. This was repeated until the coil fell in this position.

The explanation of this is given in Threlfall's paper (*l. c.*), in which it is shown that at small inductions the tractive force is less when the two-pole-faces are everywhere in contact than when they are separated at one side, thus enclosing a wedge-shaped gap.

This was the case in the present experiments up to inductions of about 14,000 C.G.S.

For higher inductions the tractive force is greatest when the surfaces are everywhere in contact, the upper core and coil therefore assuming naturally the proper position, provided, of course, the screw-adjustment is first sufficiently good. For inductions up to about 14,000 C.G.S., therefore, the lower bar was in unstable equilibrium when in good contact with the upper, for higher inductions in stable equilibrium; at about 14,000 the equilibrium was indifferent, and the nature of the contact was found within wide limits to have no influence on the Tractive Force.

As regards the results showing better agreement with the theory than before at higher inductions, I attribute this to a better method of testing the screw-adjustment of the upper coil, and partly, perhaps, to the improved state of the contact-surfaces after polishing.

At this stage the weights were all smaller than those calculated from Maxwell's expression, but their square roots were approximately proportional to the induction for inductions up to about 14,000 units, being still smaller at higher inductions, the deviation from the theoretical values increasing to about 3 per cent. at $B=20,000$.

The uniformity of these results led me to believe that the errors, if any existed, were not accidental but due to some cause which acted always in the same way. Accordingly, I tried the effect of *increasing* the distance between the coils, thus leaving a greater part of the core near the plane of contact unsurrounded with coil-windings. I found that the effect of increasing this distance by about 2 millim. was very slight for inductions up to about 14,000 C.G.S., and for higher inductions was a diminution of Tractive Force of a few hundred grammes, varying with the induction—differences of the same order as the differences between the above observed and calculated values. I could also increase the Tractive Force by an amount of the same order by putting between the coils a few extra turns of wire. As the actual distance between the windings of the two coils (including the end-plates and the space occupied by the small guiding ring) in the above experiments was about 5 millim., it was clear that the observed weights were on this account smaller than the theoretical values; in other words, that the induction, as calculated from the magnetization-curve, was greater than the actual induction across the surface of contact.

This result can be easily explained; for when the induction is low the permeability of iron is great, and the tubes of induction pass more readily through the iron; but when the induction is high and the permeability small the absence of coil-windings near the surface of contact causes a greater proportion of tubes to pass out into the air; in other words, causes a greater spreading of the tubes. The effect of the absence of a given number of turnings near the plane of section might be calculated [see Neumann: "Ueber die Magnetisirung eines Drehungsellipsoids," *Crelle*, Bd. xxxvii. (1848)], but it was deemed better first to diminish the gap between the coils as much as possible. With this object the coils were somewhat altered, the end-plates being altogether removed and the small guiding ring being let into one of the coils. The gap-width could then be reduced to zero, but a width of about 1·5 millim. was necessary in order to examine the contact of the pole-faces. The effect of this was to increase the Tractive Force by several hundred grammes at all inductions, the increase being greatest at high inductions. The magnetization-curve was carefully re-determined and the results calculated out as before. The attraction of the coils alone was also remeasured, but found not to have been appreciably increased by the shortening of the gap.

Final Results.

The results now agreed with Maxwell's theory to one-half per cent. for inductions up to 19,000 units, but between 19,000 and 20,000 units the square roots of the observed weights are rather more than 1 per cent. below the calculated values.

This difference at high inductions might well be due to the fact that there was still a gap of 1·5 millim. between the coils, which would have a spreading effect at high inductions; to the effect of the stress on the magnetization; or to temperature effects, the coils being considerably heated by a current of 10 amperes. A better agreement with the theory was therefore hardly to be expected.

No readings could be taken at inductions below 6000, since the weight of the lower coil and half-core was sufficient to overcome the stress at this induction. The following table gives the values of the intensity of magnetization, induction, and the square roots of the theoretical and observed Tractive Forces measured in grammes weight; and the diagram (fig. 2) shows the values of the Induction and the square root of the observed Tractive Force, the theoretical values being represented by the straight line whose inclination is determined by the factor

$$\sqrt{\frac{A}{8\pi g}}\,.$$

Intensity of Magnetization. I. C G.S.	Induction. B. C.G.S.	Square root of number of grams. supported.	Calculated value of square root of Tractive Force.
493	6198	52·10	52·06
551	6929	59·05	58·40
646	8122	68·61	68·55
853	10726	90·86	90·59
996	12517	105·00	105·60
1163	14635	122·30	123·50
1291	16261	136·80	137·30
1346	16975	142·60	143·20
1400	17690	148·7	149·30
1463	18545	155·8	156·50
1550	19729	164·2	166·60
1585	20234	168·4	170·80

Fig. 2.—Soft iron Ellipsoid of Revolution cut in equatorial plane and interface polished. Area of surface of contact = 1·767 square centim.

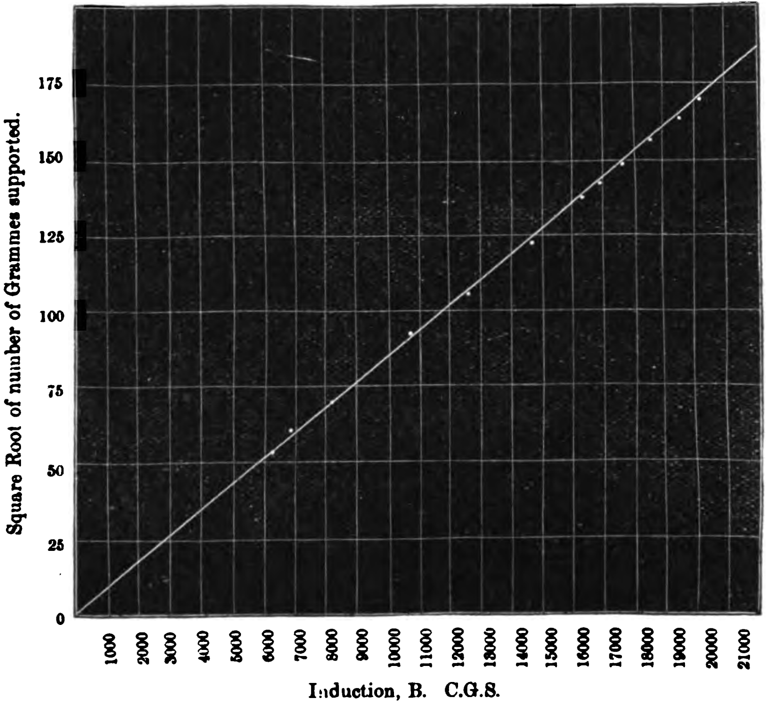

Fig. 3.—Soft iron Ellipsoid of Revolution. Length (after cutting) = 22·493 centim. Least diameter = 1·5 centim. Surfaces of contact plane and polished.

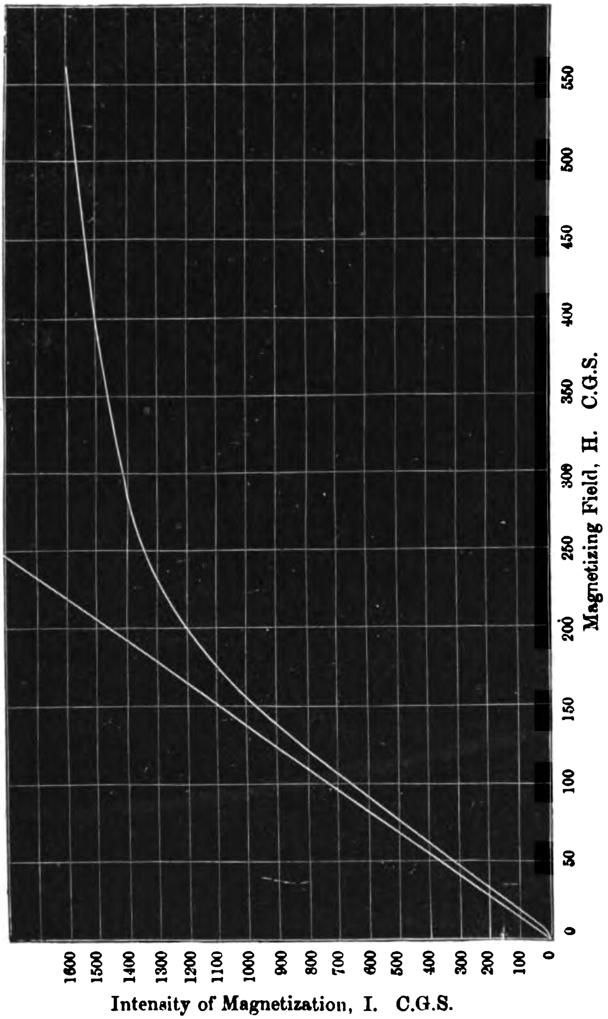

Fig. 3 represents the magnetization-curve and the demagnetizing force of the ellipsoid.

Each observation was repeated several times, and the mean value taken as the true value. The weights, however, never differed by more than 1 or 2 per cent. for the same magnetizing current.

It appears therefore that the present method of measurement has great advantages over the ballistic method used by Bosanquet and Threlfall, for Bosanquet obtained sometimes for the same induction weights differing by nearly 20 per cent.

The apparatus as above described (or any apparatus of the S. P. Thompson's "permeameter"* type) may therefore be used for the *accurate* measurement of magnetic induction in uniformly magnetized bars, the essential conditions being that the contact surfaces are plane, that the upper bar can be finely adjusted in position and very rigidly fixed, and that the contact surfaces are as nearly as possible flush with the ends of the magnetizing-coils, space being left for the small guiding-ring on one of the bars. The lower bar must also be guided, and for this it is sufficient that its lower end pass freely through a ring properly adjusted in position.

A few experiments were made with the half-cores separated by very thin sheets of silver. Two sheets were used, of thicknesses 1·5 and 8 hundredths millim. respectively, and it was found that the introduction of a sheet always caused a diminution of both magnetization and tractive force, greater with the thicker sheet. No increase similar to that found by Wassmuth† at low inductions was observed.

In conclusion, I wish to express my obligations to the late Prof. Kundt and Drs. du Bois and Rubens for the interest they took in my work, and the help they gave me in various ways.

Berlin Phys. Inst. d. Univ.,
Jan. 1895.

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* Journ. Soc. Arts, Sept. 12, 1890.

† *L. c.* p. 336.

XXV. *On the Influence of the Dimensions of a Body on the Thermal Emission from its Surface. By* ALFRED W. PORTER, *B.Sc., Demonstrator of Physics, University College, London*[*].

IN discussing the rate at which heat passes outwards from a conducting body into the medium in which it is immersed, it is usually assumed that (for small excesses of temperature of the body above its surroundings) it may be taken as proportional to the excess of temperature. This law is followed, as far as is known, if the body is in a vacuum and loses heat simply by radiation between its own and surrounding surfaces. If, however, it is immersed in a medium, such as air, which carries away heat by conduction and convection as well as by radiation, the problem becomes more complicated, and to assume that the whole effect may be treated as radiation only does not give results which are even an approximation to those obtained experimentally. For example, on this assumption the amount passing outwards from unit area of the surface per second per unit excess of temperature (*i. e.* the "emissivity") should be independent of the size of the body. Results obtained by Péclet from experiments on cylinders and spheres of different sizes show that this constant depends materially upon the sizes of the bodies experimented upon. Péclet's formulæ connecting the rate of emission (exclusive of the radiation effect) with the radius (r) for 0° C. excess are :—

For a horizontal infinitely long cylinder of brass . . . . $2{\cdot}058+\dfrac{{\cdot}0382}{r}$

For a sphere . . . . $1{\cdot}774+\dfrac{{\cdot}13}{r}$

in which kilogrammes, metres, hours are the units employed. Other formulæ are given by him which it is unnecessary to quote here.

These results do not seem to have attracted much notice, as they are not given in any of the text-books of Physics. They do, however, appear in a book compiled for practical men by Box[†], from which the formula for the sphere is quoted, on

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[*] Communicated by the Physical Society: read January 11, 1895.

[†] 'A Practical Treatise on Heat for the use of Engineers and Architects,' by Thomas Box. (London, E. and F. N. Spon, 2nd edition, 1876.) This book does not appear to be generally known to physicists; and, judging from recent references to it, I gather that still less is it realized that the author's data are to a great extent obtained from Péclet, although he states the source to which he is indebted in his preface.

Professor Ayrton's authority, in Everett's 'Illustrations of the C.G.S. System of Units' (1891 edition, p. 133) *.

Experiments on thin wires by Messrs. Ayrton and Kilgour have confirmed the fact that the emissivity can be expressed empirically through a considerable range of radius in the form given by Péclet; and experiments on rods which have been in progress in this Laboratory since 1891, an account of which was read by Mr. Eumorfopoulos before the Physical Society on the same day as this paper, lead to the same conclusion.

It was these that first called my attention to the subject; and in order to account approximately for them and the results elsewhere obtained, I propose here to examine the results of supposing the loss to only in part follow the law of radiation, the remainder being assumed to follow the law of conduction.

The rate of loss due to radiation will be proportional to the excess of the temperature of the body above that of its enclosure, and if we reckon temperatures from that of the enclosure, we may write the rate due to this cause

$$h\,\theta_a,$$

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* A mistake occurs in Everett as well as in a paper on the same subject published later by Professor Ayrton and Mr. Kilgour in the Phil. Trans. for 1892, in which Everett's statement is quoted. The formulæ are given in Box as

$$\cdot 421+\frac{\cdot 307}{r} \text{ for the cylinder}$$

and

$$\cdot 3634+\frac{1\cdot 0476}{r} \text{ for the sphere,}$$

in which the units are the pound, foot, and hour, *the radius being however in inches.*

Translated into C.G.S. units, they become

$$\text{Cylinder:}\quad \left[\cdot 572+\frac{1\cdot 061}{r}\right]\times 10^{-4},$$

$$\text{Sphere:}\quad \cdot 00004928+\frac{\cdot 0003609}{r}.$$

In Everett, and in Ayrton and Kilgour's paper, the latter appears as

$$\cdot 0004928+\frac{\cdot 0003609}{r}.$$

Further, it is not clear from Everett whether the formula he gives refers to air-effect *plus* radiation or to one of these alone. The specification of "blackened sphere" would lead one to suppose that either the total effect or else the radiation only is meant, since the air-effect has been shown to be independent of the *nature* of the surface. On reference to Péclet, the formula is seen to represent the *air-effect alone.*

where h is the radiation-constant and θ_a is the temperature at the surface of the body.

The remainder, which is to include both true conductive and also convective loss, will be proportional to the temperature-gradient in the medium close to the surface of the body. It may on this assumption be represented by

$$-c \left.\overline{\frac{d\theta}{dr}}\right|_a,$$

where $\left.\overline{\frac{d\theta}{dr}}\right|_a$ is the temperature-gradient in the medium at the bounding surface of the body, and c is a positive constant which will be referred to as the convection-conductivity.

The total rate of loss is hence

$$h\theta_a - c \left.\overline{\frac{d\theta}{dr}}\right|_a,$$

which may be written

$$\left[h - c\frac{\left.\overline{\frac{d\theta}{dr}}\right|_a}{\theta_a}\right]\theta_a.$$

The expression inside the brackets is the quantity called the "emissivity" in the usual treatment of the problem. On the above assumption, far from being a constant, it is seen to be a thing whose value will vary with every modification of the experiment by which it is sought to be determined.

To fix ideas, take the case of a cylindrical rod or wire of radius "a" heated uniformly at all points and maintained at constant temperature by mechanism the nature of which is of no consequence. Let it be surrounded by a coaxal cylindrical sheath of radius R maintained at a constant temperature, which will be taken as the zero of temperature, the intervening space being filled with conducting or pseudo-conducting material. The differential equation to be satisfied by the temperature in the medium is

$$\frac{d^2\theta}{dr^2} + \frac{1}{r}\frac{d\theta}{dr} = 0,$$

since with the above conditions everything is symmetrical with regard to, and uniform parallel to, the axis of the cylinder; and the solution of this which satisfies the boundary conditions is

$$\theta = \theta_a \frac{\log \mathrm{R} - \log r}{\log \mathrm{R} - \log a};$$

whence the emissivity (e) becomes

$$h + \frac{c}{a(\log \mathrm{R} - \log a)},$$

or for convenience of calculation,

$$h + \frac{b}{a(\log_{10} \mathrm{R} - \log_{10} a)}.$$

This, then, is presumably an approximation to a theoretic formula for the case of experiments like those of Messrs. Ayrton and Kilgour referred to before; and the accompanying Table I. and curves (fig. 1) (pp. 272 & 273) show how closely, by a suitable choice of constants, it can represent the experimental values. The constants I determined by the method of least squares; this I considered it advisable to do, because the experimental values are not sufficiently precise to enable one to draw a smooth curve through them with anything like certainty. In particular I may mention that their own empirical formulæ fail to fit in with the experimental values yielded by the wire of radius ·0037; and these values are similarly shunned by the formulæ which I give.

The first term in each of my formulæ should represent the radiation-constant. It must be noted, however, that for such very thin wires radiation forms only a small portion of the whole emission; and therefore, without having results of greater accuracy from which to deduce the formulæ, it is not possible to assign the value of this term with definiteness. All the values for it are, however, higher than those obtained by observers who have experimented on the emission from surfaces *in vacuo*, as the following data show:—

Radiation Values.

Quoted from Everett.	**Bottomley: Sooted globe in Sprengel vacuum**	·000125	for excess of	83°·6.
		·000095	,, ,,	32°·7.
	Bottomley: Silvered and highly polished globe	·0000354	,, ,,	72°·1.
		·0000296	,, ,,	43°·7.
	Nichol (published by Tait): Pressure of air = 10 mm. of mercury	·000057	,, ,,	42°.

As regards the other constant "b" ($= {\cdot}4343\,c$), we have

At 300° . . $b = {\cdot}0696 \times 10^{-3}$, $c = {\cdot}16 \times 10^{-3}$,
200° . . $b = {\cdot}0620 \times 10^{-3}$, $c = {\cdot}143 \times 10^{-3}$,
150° . . $b = {\cdot}0605 \times 10^{-3}$, $c = {\cdot}139 \times 10^{-3}$,
100° . . $b = {\cdot}0549 \times 10^{-3}$, $c = {\cdot}126 \times 10^{-3}$.

TABLE I.—Thermal Emissivities of Wires at different Temperatures obtained experimentally by Messrs. Ayrton and Kilgour, compared with calculated Values.

a. Radius of wire, in centimetres.	Temperature 300°.			Temperature 200°.			Temperature 150°.		Temperature 100°.		
	Experimental values ×10³.	Values calculated from		Experimental values ×10³.	Values calculated from		Experimental values ×10³.	Values calculated from formula given in this paper.	Experimental values ×10³.	Values calculated from	
		Ayrton and Kilgour's formula.	Formula given in this paper.		Ayrton and Kilgour's formula.	Formula given in this paper.				Ayrton and Kilgour's formula.	Formula given in this paper.
·00155	14·40	14·54	14·69	12·78	13·03	12·80	11·87	12·30	10·85	11·04	11·22
·00255	9·85	9·18	9·39	9·07	8·26	8·47	8·60	8·07	7·90	7·07	7·38
·00370	5·84	6·68	6·92	5·38	6·04	6·27	5·09	5·92	4·55	5·20	5·43
·0076	3·84	3·82	3·92	3·46	3·49	3·59	3·21	3·31	2·93	3·05	3·06
·0103	3·35	3·12	3·12	3·08	2·88	2·88	2·94	2·61	2·80	2·53	2·43
·0118	2·84	2·86	2·83	2·59	2·65	2·61	2·45	2·36	2·30	2·33	2·19
·0141	2·61	2·58	2·48	2·36	2·40	2·31	2·22	2·06	2·05	2·12	1·93
·0178	2·29	2·28	2·11	2·14	2·13	1·96	2·03	1·73	1·80	1·90	1·63
	Formulæ referred to above. Ayrton and Kilgour's:— $e = ·001135 + \frac{·016084}{D}$, where D is diameter in mils. Formula from which the last column is calculated:— $e = \left[·29 + \frac{·0696}{a \log\left(\frac{2·54}{a}\right)}\right] \times 10^{-3}$.			Formulæ referred to above. Ayrton and Kilgour's:— $e = ·001111 + \frac{·014303}{D}$, where D is diameter in mils. Formula from which the last column is calculated:— $e = \left[·36 + \frac{·0620}{a \log\left(\frac{2·54}{a}\right)}\right] \times 10^{-3}$.			No formula given by Ayrton and Kilgour. Formula from which the second column is calculated:— $e = \left[·16 + \frac{·0605}{a \log\left(\frac{2·54}{a}\right)}\right] \times 10^{-3}$.		Formulæ referred to above. Ayrton and Kilgour's:— $e = ·001036 + \frac{·012078}{D}$, where D is diameter in mils. Formula from which the last column is calculated:— $e = \left[·20 + \frac{·0549}{a \log\left(\frac{2·54}{a}\right)}\right] \times 10^{-3}$.		

Fig. 1.

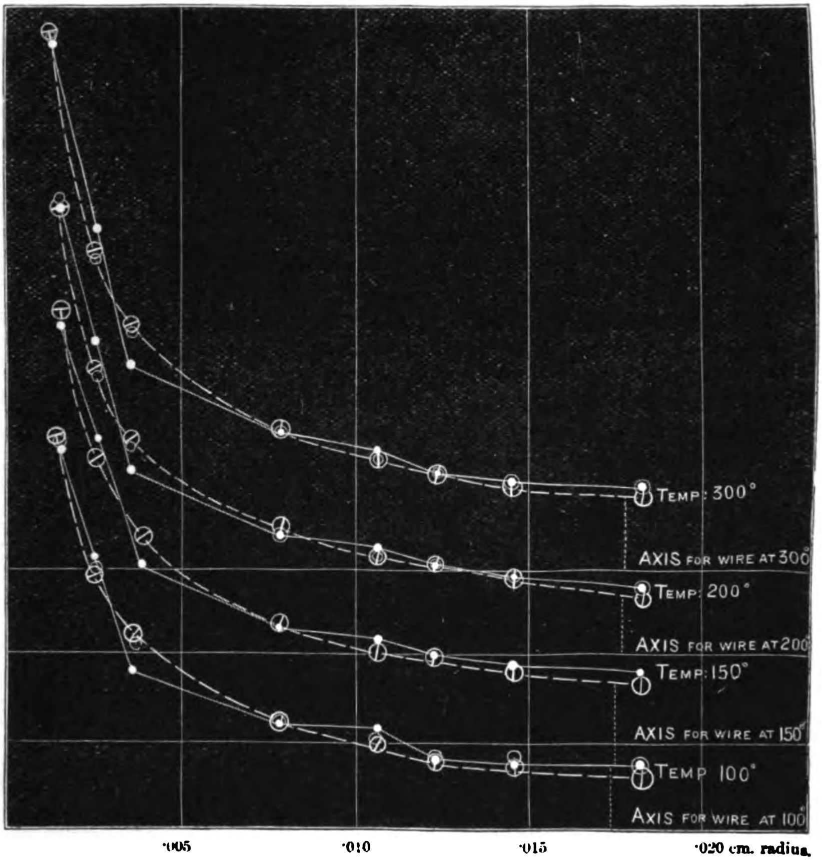
Thermal Emissivities of Wires at Different Temperatures.

Ordinates represent Emissivities.
Abscissæ represent Radii of Wires.

Messrs. Ayrton and Kilgour's Experimental Values indicated thus: —●————●—

Points on their Empirical Curves indicated thus: ⊙

Curves represented by formulæ given in this paper indicated thus: –⊕– – –⊕–



Péclet's results were derived from experiments on five cylinders: only two of them are available for my purpose, since the others were either of different material or different surface. They were short cylinders of unpolished brass, terminated by hemispherical ends, allowance for which was made from the experiments on spheres. Péclet, therefore, considered his results to apply to infinitely long cylinders. Their radii were 5·1 and 6·9 cm. respectively, and measurements were made on them in a cylindrical enclosure 40 cm. radius and 100 cm. long. His results are:—

Radius.	Experimental results.
5·1	·0000867
6·9	·0000803

and the formula which I derive from these is

$$e = \cdot 0000383 + \frac{\cdot 00022}{a(\log_{10} 40 - \log_{10} a)}.$$

In large cylinders like these radiation plays a more conspicuous part, and the value of the first term in my formula which represents it is in very good accordance with values obtained by direct methods. The value of "b" is, however, very different from that obtained from Ayrton and Kilgour's experiments; and the conclusion is forced upon one that although to consider "b" a constant may serve as long as the enclosure remains the same, it will by no means suffice to take it the same constant under such widely different conditions as obtain in these two sets of experiments. The character of the convective flow is evidently totally different in the two cases.

The same conclusion is arrived at by an examination of results obtained from experiments on spheres. The formula for a sphere, found by means of the same assumption as before, is

$$e = h + \frac{cR}{a(R-a)}.$$

Péclet experimented on three spheres in the same enclosure; and assuming the enclosure to behave like a spherical one of 45 centim. radius, the formula becomes

$$e = \cdot 00003845 + \frac{\cdot 000417 \times 45}{a(45-a)}.$$

The experimental and calculated values are here given:—

Radius in centim.	Experimental value of *e* for 0° excess.	Calculated value from above formula.	Calculated by Péclet's own formula for air-effect and adding radiation.
7·465	·0001051	·0001054	·0001048
10·58	·0000898	899	906
15·38	·0000801	796	800

It will be observed that the radiation-constant is practically the same as that derived from his cylinder results*, while the value of c is rather less.

Experiments on spheres (both of 2 centim. radius) have also been made by MacFarlane† and extended by Bottomley‡, both using the same enclosure, which was of "large dimensions" (*Bottomley*).

Extrapolation from Péclet's results for a sphere of 2 centim. radius in his enclosure gives:—

Using his formula.	Using formula given above.
·000237.	·000256

MacFarlane's results for a blackened sphere (Péclet's were dull) give ·000238 for 0° excess. Bottomley's results give about ·000260 for 0° excess, showing that the formula derived from Péclet's results is roughly applicable here.

Bottomley also experimented on the same sphere in a spherical enclosure of 5 centim. radius. If the formulæ hitherto given in this paper were applicable to this case, the emissivity ought to increase with decrease of radius of enclosure. Bottomley's results show a marked *decrease*. The value at 17° for 0° excess is not more than ·00011 after correcting approximately for temperature.

Since the true radiation was determined separately it is possible to find the value of "c" for these experiments, although only one sphere was employed. I subjoin a table:—

---

* Péclet endeavoured to estimate the radiation independently by means of a thermopile, and deducted it from the total emission to obtain the air-effect. The value he obtained was only ·0000072 for 0° excess, a value so much smaller than received values that I have ignored it entirely, and dealt only with the total effect.

† D. MacFarlane, Proc. Roy. Soc. 1892.

‡ J. T. Bottomley "On Thermal Radiation in Absolute Measure," Trans. Roy. Soc. 1892.

From	*c.*
Péclet's results from spheres	·000417.
MacFarlane's and Bottomley's results in *large* enclosure, assuming Bottomley's value for radiation ...	about ·0004.
Bottomley's results for sooted sphere in small enclosure	·000192 for excess of 85° C. 181 ,, ,, 65° C. 168 ,, ,, 45° C. 160 ,, ,, 35° C.
Bottomley's results for silvered and highly polished sphere in small enclosure	·000168 for excess of 65° C.

Place against these the values obtained from cylinders:—

From	*c.*
Péclet's results in large enclosure ...	·000508 for 0° excess.
Ayrton and Kilgour's, in enclosure of 2·54 centim. radius	·000160 with wire at 300° C. 143 ,, ,, 200° C. 139 ,, ,, 150° C. 126 ,, ,, 100° C.

In order to throw light on this question, I have started experiments, in conjunction with Mr. Eumorfopoulos, on cylindrical rods in cylindrical enclosures of different radii. Experiments made so far are as follows:—

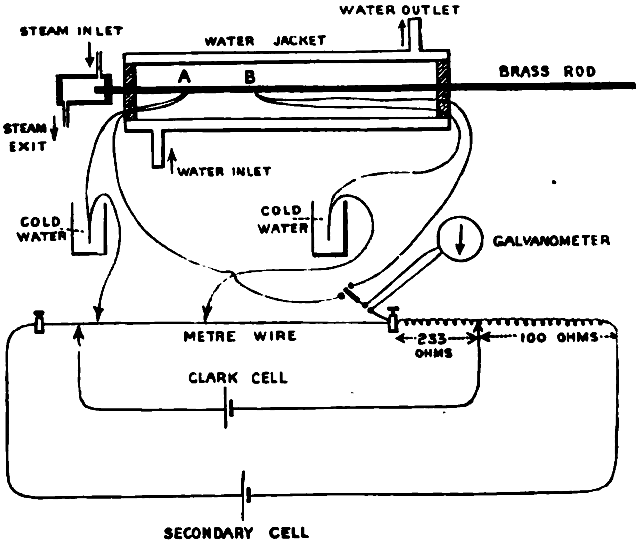
A brass rod ·483 centim. radius has soldered on it *two* thermoelectric junctions of iron and german-silver at a distance apart of 10 centim., each of which is part of a couple whose other junction is kept cold in a water-pot. The rod is heated at one end by steam until the steady state of temperature is attained, and the ratio of the temperatures (reckoning from enclosure temperature as zero) of the two junctions is measured successively with different water-jackets embracing the rod.

The general arrangement is shown in fig. 2 (p. 277). Tap-water is passed through the water-jacket at such a rate that its temperature as it enters is sensibly the same as when it leaves the jacket. This temperature is read by a thermometer, as also are the temperatures of the cold junctions. Then either the junction at A and its corresponding cold junction, or the junction at B and its corresponding cold junction, can be connected to a potentiometer, and the thermoelectric E.M.F. in each case determined.

The potentiometer was standardized from time to time by a Clark's cell which is so connected (switches not shown) that the same galvanometer does for all three operations.

The ratio of the thermoelectric E.M.F.'s is approximately the same as the ratio of the excess temperatures of the points A and B after it has been corrected for slight differences of temperature between the two water-baths and the water-jacket. Two jackets have been employed so far, and compared with each other and with the bar unjacketed. In this last case the bar is merely shielded from the ruder form of draught by brown-paper screens.

Fig. 2.



The results are given in the subjoined table:—

R. Inner radius of enclosure in centim.	Excess temperature of A. θ_A.	Excess temperature of B. θ_B.	Average excess.	Emissivity at stated mean excess temperature.	Emissivity approximately corrected to one temperature.
Indefinitely great.	54·0	30·5	42·2	·0001882	·000191
5·15	57·0	33·3	45·3	·0001610	·000162
1·6	61·1	36·6	48·8	·0001514	·000151

The values of emissivity here given have been calculated from the formula

$$e = \frac{kr}{2}\left[\frac{\log \theta_A - \log \theta_B}{\cdot 4343 \times x}\right],$$

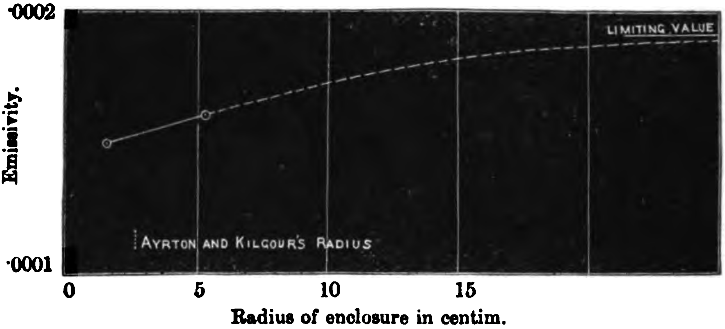
in which $x=10$ centim., and the value of k taken is that determined by Mr. Eumorfopoulos for the same rod by Ångström's method, viz. ·2386. The emissivity is therefore in each case an average value for the range of temperature between the two points. The actual temperatures were ascertained by standardizing the thermoelectric couples in water-baths of known temperatures.

The above results are also shown plotted in fig. 3. An elastic curve (bent steel lath) has been made to pass through the two results for definite dimensions and extended provisionally by a dotted line so as to rise asymptotically to the highest value. It is unsafe to rest too much upon these few results: more will need to be obtained before the law of variation can be stated with certainty: the following paragraph must be considered therefore as merely provisional. Take the two definite values and also (by *inter*polation) the value for an enclosure of 2·54 centim. radius (that employed by Messrs. Ayrton and Kilgour) and find the values of "*b*." They are:—

Fig. 3.

Variation of Emissivity of Cylindrical Brass Rod with the Radius of its Cylindrical Enclosure.

Radius of rod = ·483 centim.



Radius of enclosure. R.	Radius of rod. *a*.	*b*.
1·6	·483	$\cdot 029\times 10^{-3}$
2·54	·483	·0418 ,,
5·15	·483	·0643 ,,

The value derived from A. and K.'s results at 60° is

$\cdot 047 \times 10^{-3}$. As their thin wires blocked up the enclosure less than the thick rod here employed, it is natural that the value obtained from them should be greater than that given above.

The formula which I have given for a cylinder appears to hold through a far wider range than that given by Messrs. Ayrton and Kilgour. Take for example their formula for a wire at 100°. The emissivity for it can never (for any radius) fall lower than

$$\cdot 00107.$$

Calculating from my formula we get

$$\cdot 00036$$

for a rod of ·483 centim. radius at 100°. On reduction to 60° it becomes about

$$\cdot 00025,$$

which is much more within sight of the value ·000154 which is obtained from fig. 3. Considering the violent nature of the extrapolation here made, the agreement is probably as close as could reasonably be expected.

Conclusions.

i. That the theoretic assumption made in this paper gives results which are accordant through a wide range of radius of rod with experimental results obtained under similar conditions as regards enclosure: and in this respect is far superior to the usual assumption which gives no account whatever of variation of the value of emissivity with radius.

ii. That if the freedom permitted to convection effects be varied, as it will be if the enclosure be changed, it is necessary to consider the convecto-conduction constant as varying with the changed conditions according to a law which can only be found by a complete series of experiments made with enclosures of different dimensions.

iii. I conclude that the enclosing boundary is as important a factor in determining the value of the emissivity as the size of the body itself: and that therefore in any collection of data (such as Everett's) it is very necessary to specify the exact nature of the enclosure in which the experiments were conducted; and, further, that all determinations that have been made of this constant and published with imperfect description of all the boundaries are of little scientific value.

Finally, I must express my thanks to Prof. G. C. Foster for kindly advice and suggestions given from time to time in connexion with this matter.

University College, London,
January 1st, 1895.

XXVI. *On the Determination of Thermal Conductivity and Emissivity.* By N. Eumorfopoulos, *B.Sc., Demonstrator in Physics, University College, London*[*].

If a long metallic bar of uniform cross-section be heated at one end, and be left long enough to acquire a steady state, the distribution of temperature along it is usually expressed by

$$u_x = u_0 e^{-x\sqrt{\frac{hp}{ks}}},$$

where u_x is the excess of temperature over surroundings of a point on the bar at a distance x from the point whose excess of temperature is u_0, x being measured positively along the direction of decreasing temperatures;

h and k are the emissivity and conductivity respectively;

p is the periphery of the bar, and s the cross-section.

If the bar be of circular cross-section and r its radius, the above expression reduces to

$$u_x = u_0 e^{-x\sqrt{\frac{2h}{kr}}};$$

that is, if two bars have at one point of each the same temperature u_0, they will also have the same temperature u_x at distances x_1 and x_2 respectively, measured from these points, and such that

$$x_1\sqrt{\frac{h_1}{k_1 r_1}} = x_2\sqrt{\frac{h_2}{k_2 r_2}}.$$

If the bars are of different radii, but of the same material, and we accordingly write $h_1=h_2$ and $k_1=k_2$, we get

$$\frac{x_1}{x_2} = \sqrt{\frac{r_1}{r_2}}.$$

Some time ago Prof. G. C. Foster suggested to me, as a laboratory exercise, to undertake the verification of this relation.

The method adopted was to heat the ends of two such rods in steam until they had acquired the steady state, and then by means of two thermoelectric joints (one on each rod) to find a series of isothermal points.

With two *brass* rods of radii $r_1=3{\cdot}4$ and $r_2=2{\cdot}6$ mm. respectively, the distances at which equal temperatures were found were as follows :—

---

[*] Communicated by the Physical Society: read January 11, 1895.

$$\sqrt{\frac{r_2}{r_1}}=0\cdot87.$$

x_1.	x_2	$\frac{x_2}{x_1}$
20 mm.	13 mm.	·65
40	29	·72
60	42	·70
85	64	·75
110	78	·71

Mean = ·71

Similar experiments with *copper* rods gave :—

$$r_1=3\cdot35 \text{ mm.}, \quad r_2=2\cdot45 \text{ mm.} \quad \sqrt{\frac{r_2}{r_1}}=0\cdot86.$$

x_1.	x_2.	$\frac{x_2}{x_1}$.
20 mm.	18 mm.	·90
40	25	·62
60	34	·57
80	47	·59
100	61	·61

In the first value of $\frac{x_2}{x_1}$ some error has, no doubt, crept in.

Mean of last four = ·60.

Another set of experiments with the same rods gave :—

x_1.	x_2.	$\frac{x_2}{x_1}$.
20 mm.	10 mm.	·50
40	22	·55
20	11	·55
40	22	·55
20	12	·60

Mean = ·55

To ascertain whether the copper rods really consisted of the same metal, their specific electrical resistances were compared. The result was

$$\frac{\rho_1}{\rho_2}=\cdot80.$$

Assuming that the ratio of thermal conductivities was the same as that of electrical conductivities, this gives

$$\frac{x_2}{x_1}=\sqrt{\frac{k_2r_2}{k_1r_1}}=\cdot77$$

as the calculated ratio of the distances at which equal temperatures should be found, instead of ·60 and ·55, the mean ratios actually found in the two sets of experiments already mentioned.

In order to test the trustworthiness of the method employed, one of the above rods was heated in the middle under the same conditions as before, and isothermal points found on each side of the heated portion. The results were satisfactory, as the following numbers show :—

x.	x_2.
20 mm.	19 mm.
40	40
60	61
80	81

At this point the experiments were abandoned for a time. They were subsequently resumed, when a Bunsen burner was used as the source of heat, in order to have a greater range of temperature. In the experiments mentioned before, and also in these, no screens were employed, a sheltered part of the laboratory being used. The following are some of the results obtained :—

German Silver Rods.

$$r_1=3{\cdot}0 \text{ mm.},\quad r_2=2{\cdot}5 \text{ mm.},\quad \sqrt{\frac{r_2}{r_1}}={\cdot}91.$$

Making $x_2=10{\cdot}3$ cm., $x_1=11{\cdot}95$ cm. as a mean of five determinations, or

$$\frac{x_2}{x_1}={\cdot}86.$$

As a mean of a large number of experiments, making $x_2=10{\cdot}0$ cm., x_1 was found to be $11{\cdot}68$ cm., or

$$\frac{x_2}{x_1}={\cdot}86.$$

The arrangements were then slightly changed, so as to experiment on a hotter part of the rod, with the following result as a mean of a series of experiments :—

$x_2=10{\cdot}0$ cm., $x_1=11{\cdot}86$ cm. ; or

$$\frac{x_2}{x_1}={\cdot}84.$$

The ratio of specific electrical resistances for these rods was found to be ·95; assuming this as the ratio of k_2 to k_1, we get

$$\frac{x_2}{x_1}=\sqrt{\frac{k_2r_2}{k_1r_1}}=0\cdot89,$$

the mean result found by experiment being 0·85.

It is to be noted that there is not so much difference between the radii of the two rods as there was in the other cases.

Brass Rods, being the rods previously experimented on.
$x_1=65$ mm.;
$x_2=47\cdot3$ mm. (mean of three determinations).

$$\frac{x_2}{x_1}=\cdot73,\quad\sqrt{\frac{r_2}{r_1}}=\cdot87.$$

Copper Rods, previously used.
$x_1=60$ mm.;
$x_2=33$ mm. (mean of three determinations).

$$\frac{x_2}{x_1}=\cdot55,\quad\sqrt{\frac{r_2}{r_1}}=\cdot86.$$

Brass Rods. These are two new rods, which were used in experiments to be described later.

$$r_1=3\cdot21\text{ mm.},\quad r_2=1\cdot69\text{ mm.},\quad\sqrt{\frac{r_2}{r_1}}=\cdot73.$$

As a mean result of a series of experiments, for $x_2=5$ cm., x_1 was found to be 7·96 cm.; or

$$\frac{x_2}{x_1}=\cdot63.$$

It must be pointed out, however, that with the Bunsen burner the parts of the rod nearest the flame become visibly oxidized, this being especially noticeable in the case of the thicker rod—so much so that the increased emissivity so obtained can apparently overcome the greater transmission of heat of the thicker rod. Thus, with the above brass rods, 5 cm. on the thinner rod were found equivalent in this region to 5·2 cm. on the thicker; and after the heating had continued for some time 3·7 cm. on the thicker rod balanced 5 cm. on the thinner one. The ratio given above, ·63, is for parts of the rods that were not oxidized, and did not become so after several days' heating.

The general results obtained so far are :—

Rods.	r_1.	r_2.	$\sqrt{\frac{r_2}{r_1}}$.	$\frac{x_2}{x_1}$.
Brass	3·4	2·6	·87	·72
Brass	3·2	1·7	·73	·63
Copper	3·35	2·45	·86	·57
German silver .	3·0	2·5	·91	·85

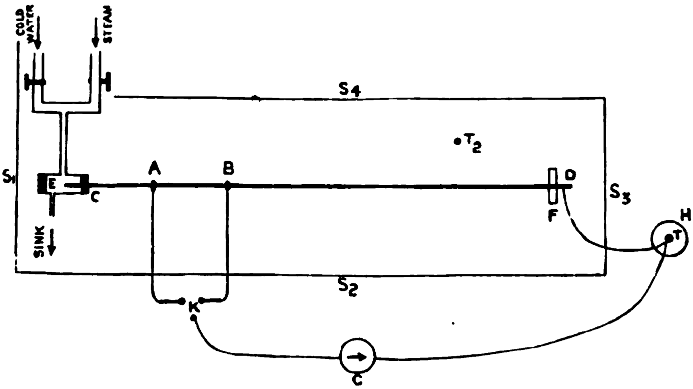
It will be seen that in every case the rate of fall of temperature along the thinner of the various pairs of rods compared is more rapid than would be inferred according to the usual formula from the distribution of temperature observed along the thicker rod. Consequently this formula cannot be legitimately used for the comparison of conductivities, unless the radii of the rods compared are equal and their surfaces in the same condition.

The only way of escaping from this conclusion is by supposing that the thermal conductivity of the smaller of each pair of rods was less than that of the thicker one. Although it seemed very unlikely that this should be so in the case of every pair, it could not be regarded as impossible. To settle the matter, it was decided to determine the absolute conductivity of at least one pair of rods.

For this purpose Ångström's method was adopted, in which one end of the rod is alternately heated and cooled, and the alternations of temperature observed at two points along the rod. Fig. 1 is a diagram of the apparatus used. C D is the rod, passing into a glass tube E, through which cold water or steam can be passed as desired. E is held up by a clamp, and F is a clamp supporting the rod at the other end, no other clamps being used for the rod. S_1, S_2, S_3, S_4 are brown-paper screens, about 2 ft. high, resting on the table and open at the top ; S_3 is about 1½ ft. wide. A and B are the two points whose temperatures have to be measured. This was done by fine iron wires passing over the rod at the required point, and held down by suitable weights. The wires pass to a key K, through the galvanometer G, to a vessel H containing cold water. H contains the other junction, and a thermometer T. A brass wire connects D to H. T_2 is a thermometer reading the temperature of the air. Both thermometers were divided into fifths and read by a telescope.

As it was not possible to keep the temperature of the air constant, allowance had to be made for the change. As the temperature required is the excess of temperature of the rod over the air, this was done by merely subtracting the temperature of the air at the given moment from that of the rod at the same moment.

Fig 1.

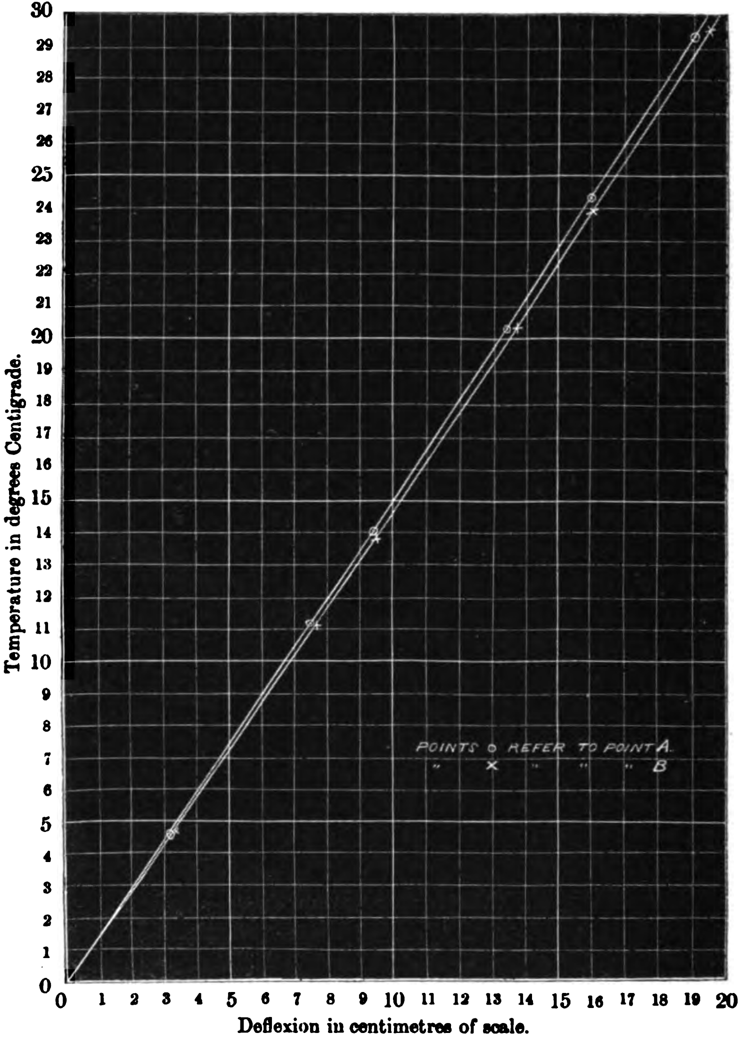


Experiment showed that it was possible to move the iron wire on the rod, and replace it, and obtain the same reading as previously; thus showing that the resistance of the joint did not appreciably alter. As the galvanometer was made somewhat sensitive, its sensitiveness was tested during the experiments by a Daniell cell passing through a large resistance (about 13,000 ohms), the E.M.F. of the Daniell being compared with that of a Clark cell. Zero readings were also taken between each deflexion. The readings of the galvanometer were afterwards standardized, a known difference of temperature being produced between the two junctions, and the deflexions observed. The following table gives an example of a standardization:—

Point A.		Point B.	
Diff. of Temp.	Galv. Defl.	Diff. of Temp.	Galv. Defl.
4·56	3·10	4·62	3·18
11·12	7·45	11·19	7·60
13·99	9·36	13·89	9·43
20·29	13·37	20·34	13·67
24·50	16·08	23·99	16·06
29·32	18·99	29·54	19·48

See fig. 2, which is plotted for these values.

Fig. 2.



When the temperature of the rod has settled down to its regular cyclic state, the excess of temperature u of any particular point at any instant t may be expressed by

$$u = a + b_1 \sin\left(2\pi\frac{t}{T} + \beta_1\right) + b_2 \sin\left(4\pi\frac{t}{T} + \beta_2\right) + b_3 \sin\left(6\pi\frac{t}{T} + \beta\right) + \ldots,$$

where T is the time-period of the alternations.

The constants a, b_1, β_1, &c. are determined by the method of least squares from the observations made.

If a, b_1, β_1, &c. and a', b_1', β_1', &c. are the constants for the two points A and B respectively, and x the distance between them, then

$$b=b'\epsilon^{gx} \quad \text{and} \quad \beta-\beta'=qx$$

(see *Ann. Chim. Phys.* lxvii., 1863).

Hence g and q can be determined, and

$$gq=\frac{n\pi}{\frac{k}{c\delta}\mathrm{T}} \quad \text{and} \quad h=(g^2-q^2)\frac{kr}{2},$$

where $n=1, 2, 3$, &c., according as you use the constants of the 1st, 2nd, 3rd, &c. sine term ;
c=specific heat of the rod ;
δ=density of the rod.

Hence k and h can be determined from each sine term. In the experiments as carried out only the first, and perhaps the third, sine terms are available for these determinations, as the others are very small, the even terms being especially so. Besides these, there is the "a" term of the above formula (the constant term of the Fourier series), which is large, and represents the mean excess of temperature of the rod. From this term we get

$$\frac{a}{a'}=\epsilon^{x\sqrt{\frac{2h}{kr}}}.$$

If we use the previously determined value of k, we can get from this equation a second value of h. This will be referred to later on.

The rods experimented upon were three brass rods (commercial specimens) of roughly ⅛, ¼, and ⅜ in. diameter ; their lengths were about 3, 5, and 6 ft. respectively. They were cleaned, but not polished. The time-period of the alternations, and the positions of A and B, were chosen so that the cycle of changes gone through should be as nearly as possible the same in the three cases.

The specific heat was determined by heating a portion of each rod to 100° in a Regnault's apparatus in the usual way. The following are the results obtained :—

Diam. of Rod	⅛ in.	¼ in.	⅜ in.
	·0937	·0943	·0945
	·0948	·0952	·0938
	·0953		·0942
Approx. rise of temp. of calorimeter . .	0·7	1·2	1·8 degr. Cent.

The mean result ·0945 was assumed for all the rods. No correction was made for change of specific heat with temperature.

The following readings are given to show how far they agree for different cycles on the same day :

Point A.				Point B.			
I. Time : $1^h\ 0^m$.	II. $3^h\ 0^m$.	III. $4^h\ 0^m$.	Mean.	I. Time : $1^h\ 30^m$.	II. $3^h\ 30^m$.	III. $4^h\ 30^m$.	Mean.
20·15	19·85	19·85	19·95	8·83	8·86	8·85	8·85
17·16	16·93	16·91	17·00	8·88	9·00	8·99	8·96
13·87	13·69	13·74	13·77	8·75	8·78	8·82	8·78
11·25	11·05	10·97	11·09	8·26	8·31	8·27	8·28
......	......	......	......	......	......	......	......
3·16	3·05	3·06	3·09	3·86	3·94	3·88	3·89
2·70	2·59	2·56	2·62	3·44	3·45	3·47	3·45
2·29	2·23	2·16	2·23	3·03	3·13	3·09	3·08
1·97	1·88	1·83	1·89	2·66	2·78	2·75	2·73

The above readings are deflexions in centimetres : 1 cm. of scale corresponds to a rotation of the magnet through 11′, or 1 cm. corresponds to a difference of temperature between the two junctions of 1½ degrees Cent.

The following expressions show the series required to fit the temperatures obtained ; they are the expressions for Set I. of Rod II., but the constants are of approximately the same magnitude with all the rods :—

$$\begin{aligned}\text{Temp. A} = {} & 13{\cdot}95 + 12{\cdot}67 \sin\left(2\pi\frac{t}{T} + 2{\cdot}1412\right) + {\cdot}42 \sin\left(4\pi\frac{t}{T} + 3{\cdot}91\right) \\ & + 2{\cdot}18 \sin\left(6\pi\frac{t}{T} + 1{\cdot}13\right) + {\cdot}18 \sin\left(8\pi\frac{t}{T} + 3{\cdot}33\right) \\ & + {\cdot}80 \sin\left(10\pi\frac{t}{T} + {\cdot}56\right) + \ldots + {\cdot}31 \sin\left(14\pi\frac{t}{T} + {\cdot}28\right).\end{aligned}$$

$$\begin{aligned}\text{Temp. B} = {} & 6{\cdot}16 + 3{\cdot}92 \sin\left(2\pi\frac{t}{T} + 1{\cdot}3806\right) + {\cdot}10 \sin\left(4\pi\frac{t}{T} + 2{\cdot}41\right) \\ & + {\cdot}38 \sin\left(6\pi\frac{t}{T} - {\cdot}40\right) + {\cdot}04 \sin\left(8\pi\frac{t}{T} + 1{\cdot}14\right) \\ & + {\cdot}07 \sin\left(10\pi\frac{t}{T} - 1{\cdot}70\right) + \ldots + {\cdot}03 \sin\left(14\pi\frac{t}{T} - 2{\cdot}68\right).\end{aligned}$$

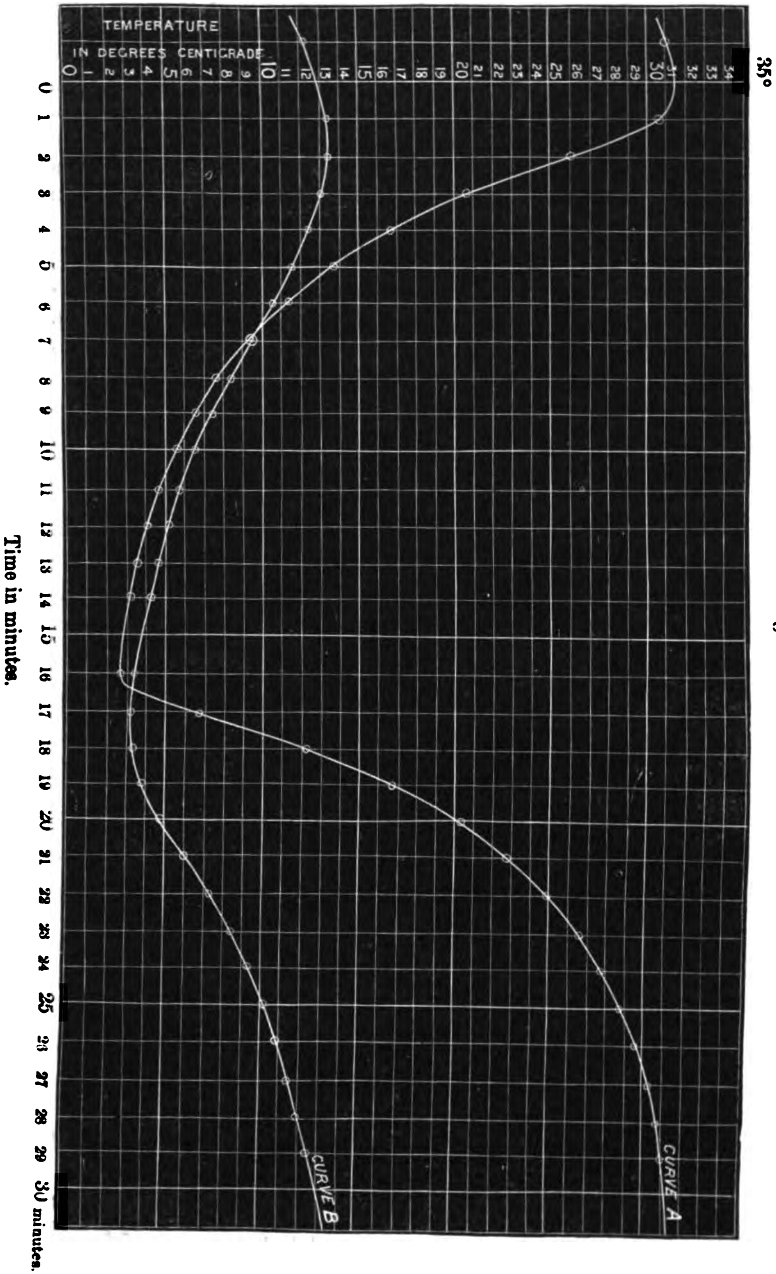

TEMPERATURE
IN DEGREES CENTIGRADE
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34
35°
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 minutes.
Time in minutes.
CURVE A
CURVE B

Fig. 3.

As an example of the curve of temperatures obtained, see fig. 3. At the abscissa marked 0 min. cold water was turned on, and at 15 min. steam. The points marked are experimental points. There are no points marked at 0 and 15 min. as I had to be in another part of the room at those instants. It will be noticed that the cold water or the steam (as the case may be) has done nearly all it can do, before the other is turned on, especially in the case of A. This can also be seen from the numbers given below.

The following are the details for each rod:—

Rod I. ($\frac{1}{8}$ inch).—Diam. = ·3377 cm. Density = 8·49. Specific electrical resistance = $7·24 \times 10^{-6}$ ohms. 7 cms. between junctions. Time-period 10 min. Determination of temperature every half-minute.

	Set I.* (Mean of 3 cycles.) Excess Temperature in degrees.		Set II. (Mean of 3 cycles.) Excess Temperature in degrees.		Set III. (Mean of 4 cycles.) Excess Temperature in degrees.	
Time in mins.	A.	B.	A.	B.	A.	B.
0	—	—	—	—	—	—
½	22·25	9·13	22·27	9·26	19·82	8·67
1	15·91	8·88	15·95	8·98	14·05	8·35
1½	10·95	7·81	11·01	7·88	9·79	7·24
2	7·90	6·58	7·87	6·50	6·72	6·00
2½	5·67	5·29	5·68	5·29	4·83	4·71
3	4·35	4·35	4·27	4·29	3·42	3·79
3½	3·32	3·52	3·30	3·49	2·61	3·06
4	2·64	2·98	2·55	2·88	1·97	2·52
4½	2·05	2·36	2·02	2·31	1·56	2·01
5	—	—	—	—	—	—
5½	1·80	1·78	1·43	1·60	1·10	1·48
6	9·11	1·65	8·63	1·56	7·46	1·42
6½	15·47	2·58	14·95	2·52	13·97	2·36
7	19·16	4·06	18·95	3·97	17·59	3·81
7½	20·91	5·42	20·77	5·40	19·42	5·10
8	22·21	6·53	22·31	6·58	20·75	6·16
8½	23·08	7·41	23·31	7·42	21·65	6·99
9	23·69	7·95	23·96	8·16	22·49	7·65
9½	24·14	8·47	24·34	8·62	22·53	8·05
Mean Temp.	27°	19½°	27°	19½°	27½°	21°
Mean Temp. Air	14°		14°		16°	

The results, in C.G.S. units, calculated from these numbers are:—

---

* At the end of this set the joint B was found displaced through about 2 mm. away from A. This introduces a possible error of about 2½ p. c. in the distance, or 5 p. c. in the conductivity, while leaving the emissivity practically unaffected.

	Set I.	Set II.	Set III.
Conductivity (from 1st sine term).	[·2407]	·2507	·2541
Emissivity:—			
From "*a*" term.	·000321	·000331	·000319
„ 1st sine term.	·000397	·000403	·000405

Set II. is probably the best of the three.

Rod II. (¼ inch).—Diam.=·6426 cm. Density=8·47. Specific electrical resistance = 7·56 × 10^{-6} ohms. 10 cms. between junctions. Time-period 20 min. Determination of temperature every minute.

	Set I. (Mean of 4 cycles.) Excess Temperature in degrees.		Set II. (Mean of 3 cycles.) Excess Temperature in degrees.	
Time in mins.	A.	B.	A.	B.
0	—	—	—	—
1	24·12	10·29	23·67	10·13
2	17·60	10·07	17·33	10·02
3	12·66	9·15	12·62	9·09
4	9·23	7·80	9·34	7·91
5	6·88	6·54	6·95	6·69
6	5·23	5·40	5·46	5·60
7	4·01	4·52	4·27	4·68
8	3·18	3·76	3·33	3·91
9	2·43	3·13	2·60	3·30
10	—	—	—	—
11	2·46	2·17	2·54	2·34
12	9·40	2·02	9·27	2·26
13	15·23	2·95	14·87	3·07
14	19·04	4·33	18·68	4·39
15	21·48	5·70	21·13	5·78
16	23·26	6·94	22·78	6·88
17	24·49	7·88	23·89	7·90
18	25·26	8·66	24·64	8·70
19	25·76	9·34	25·16	9·36
Mean Temp.......	26⅓°	18⅓°	28°	20½°
Mean Temp. Air.	12⅓°		14⅓°	

Whence by calculation:—

	Set I.	Set II.
Conductivity (from 1st sine term).	·2351	·2338
Emissivity:—		
From "*a*" term.	·000253	·000236
„ 1st sine term.	·000301	·000286

Set II. is the better of the two.

Rod III. ($\frac{3}{8}$ inch).—Diam.=·9654 cm. Density=8·49. Specific electrical resistance = 7·71 × 10^{-6} ohms. 12 cms. between junctions. Time-period 30 min. Determination of temperature every minute.

	Set I. (Mean of 3 cycles.) Excess Temperature in degrees.		Set II. (Mean of 2 cycles.) Excess Temperature in degrees.		Set III. (Mean of 3 cycles.) Excess Temperature in degrees.	
Time in mins.	A.	B.	A.	B.	A.	B.
0	—	—	—	—	—	—
1	30·85	13·15	30·83	13·21	30·15	13·02
2	25·96	13·32	26·20	13·38	25·59	13·18
3	20·86	13·05	21·15	13·14	20·57	12·92
4	16·75	12·35	17·09	12·45	16·54	12·19
5	13·52	11·36	13·91	11·47	13·41	11·19
6	11·19	10·31	11·51	10·41	11·04	10·15
7	9·28	9·27	9·55	9·34	9·11	9·15
8	7·80	8·27	7·96	8·34	7·62	8·15
9	6·57	7·32	6·74	7·45	6·37	7·26
10	5·63	6·51	5·66	6·63	5·35	6·51
11	4·80	5·77	4·81	5·85	4·50	5·72
12	4·10	5·17	4·11	5·17	3·81	5·06
13	3·60	4·64	3·55	4·60	3·25	4·49
14	3·11	4·12	3·07	4·12	2·75	3·97
15	—	—	—	—	—	—
16	2·65	3·34	2·44	3·28	2·16	3·19
17	6·67	3·07	6·59	3·08	6·29	2·92
18	12·19	3·21	12·28	3·15	11·91	3·03
19	16·75	3·87	16·85	3·81	16·44	3·67
20	20·23	4·93	20·25	4·88	19·79	4·71
21	22·83	6·10	22·81	6·03	22·40	5·85
22	24·87	7·24	24·85	7·17	24·39	7·08
23	26·45	8·28	26·43	8·25	25·97	8·07
24	27·70	9·21	27·56	9·17	27·13	9·08
25	28·68	10·03	28·44	10·04	27·90	9·89
26	29·55	10·82	29·22	10·76	28·69	10·62
27	30·10	11·37	30·04	11·30	29·25	11·24
28	30·56	11·91	30·31	11·84	29·80	11·75
29	30·97	12·37	30·77	12·35	30·17	12·19
Mean Temp.	30°	21°	31°	22°	31½°	23°
Mean Temp. Air.	13°		14°		15°	

From which by calculation we get:—

	Set I.	Set II.	Set III.
Conductivity (from 1st sine term).	·2374	·2386	·2399
Emissivity:—			
From "*a*" term.	·000208	·000208	·000205
" 1st sine term.	·000251	·000237	·000237

Set I. is the best of the three.

The third sine term is, in the case of B, too small to give reliable results, but they have been calculated in some cases, and curiously enough the conductivity always comes out lower than that given by the first term. The following have been calculated :—

	Rod I.		Rod II.	Rod III.		
	Set II.	Set III.	Set I.	Set I.	Set II.	Set III.
Conductivity—1st sine term.	·251	·254	·235	·237	·239	·240
3rd „ „	·229	·242	·233	·222	·229	·227
Emissivity — 1st sine term.	·00040	·00040	·00030	·00025	·00024	·00024
3rd „ „	·00038	·00025	·00027	·00024	·00026	·00031

Taking the mean of the chief results obtained, we get the following table :—

	Rod I.	Rod II.	Rod III.
Conductivity . . .	·2524	·2344	·2386
Emissivity :—			
From "*a*" term.	·000324	·000244	·000207
„ 1st sine term.	·000402	·000293	·000242

It hence appears that the emissivity of a body depends to a large extent on the form and dimensions of that body, and that the formula for conduction of heat along a rod, as usually given in text-books, can only be used in a very restricted sense.

It will be noticed that the two emissivities (deduced from the "*a*" term and the sine term) are to one another approximately as 1 to 1·2. The ratio appears to be too uniform to be due to accidental error of experiment, but the meaning of the two values is not quite clear. In order to obtain further information, the $\frac{3}{8}$ inch rod was heated at one end by steam under approximately the same conditions as before, and the E.M.F. of a german-silver-iron couple at different points on the rod determined by the compensation method in the ordinary way. A preliminary set was taken, which gave about the same results as the following more accurate set (readings were taken going down the rod and then going up):—

Position on rod in cm.	Bridge-Reading in cm. Down.	Up.	Mean.
0	73·8	73·7	73·75
5	53·1	52·6	52·85
10	38·0	38·0	38·0
15	27·6	27·5	27·55
20	19·8	20·0	19·9
25	14·4	14·7	14·55
30	10·6	10·8	10·7
35	7·8	7·8	7·8

Temperature of air about 10½°.

1 cm. of bridge-wire corresponds to rather less than one degree.

Dividing the above into two lots, and taking $k = \cdot 2386$, we get (this method is sufficiently accurate for this purpose):—

Mean temp.	h.
54°	·000247
42°	·000240
33°	·000231
27°	·000229

The mean temperature of the rod in the experiments by Ångström's method was about 27°, and the two emissivities found were ·000207 and ·000242, so that the steady-state emissivity comes just about halfway between the two. The rod, however, had become somewhat tarnished during the summer, and had to be cleaned again, which may or may not have made some difference. Further experiments will be needed to settle the point conclusively.

When the last part of the experiments was in progress, Mr. A. W. Porter, B.Sc., drew my attention to Messrs. Ayrton and Kilgour's paper before the Royal Society on the variation of emissivity with the diameter of the wires experimented upon. The results obtained corroborate one another, and also corroborate results that had been obtained some time ago by Péclet, and which are recorded in his *Traité de la Chaleur*. Péclet appears to have carried out a large number of experiments on emissivity, the best account of which is found in the 3rd edition (not the 4th) in vol. i. and a long note at the end of vol. iii. (published in 1860–61).

In conclusion I must express my obligations to Prof. Foster and Mr. Porter for much help given in the course of these experiments.

University College, London,
Dec. 29, 1894.

XXVII. *The Clark Cell when Producing a Current.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,

IN the Philosophical Magazine for September 1894 is a paper by Mr. S. Skinner on "The Clark Cell when Producing a Current." This paper appears to call for one or two remarks from me. Mr. Skinner says (p. 272):—"Let a cell of electromotive force E and internal resistance R have its poles joined by a wire of resistance r; then, providing R and r are constant, and there is no polarization, the potential-difference between the poles will be $\frac{rE}{R+r}$. If, however, there is polarization, then this potential-difference will be $\frac{re}{R+r}$, where e is the value of the electromotive force required to produce the observed current."

The value of $-(E-e)$ is the "electromotive force of polarization." This quantity is studied by Mr. Skinner, and its evaluation of course involves measurements of R and r. With regard to r, which appears to have been taken from a box for values down to 200 legal ohms, and for 147 legal ohms from a german-silver coil in a bath of paraffin oil, we are not given very much information. I would ask, however, whether in the light of Mr. Griffiths' experience (Phil. Trans. A. 1893, p. 401), it is safe to assume that the resistance of a coil mounted as described, and carrying a current, can be sufficiently ascertained by tests made with only a testing-current. No one ought to be more alive to this than Mr. Skinner, so that I will assume his value of r to have been sufficiently known. With regard to "R," however, the case is different. Its value was measured by Professor Macgregor's method (Trans. Roy. Soc. Canada, iii. 1882, p. 22, referred to as "by means of the commutator used by Mr. T. C. Fitzpatrick"), in which alternating intermittent currents are fed into a Wheatstone bridge, and commutated for the benefit of a galvanometer. The measurements were not made while the cell under examination was yielding a current for polarization observations: consequently the value assigned to $-(E-e)$ rests on the assumption that the resistance of the cell, while yielding a considerable current (·01 ampere) for polarization experiments, was the same as the resistance it exhibited while under test by alternating and intermittent currents. This assumption I consider to be wholly illegitimate, and to vitiate every result given by Mr. Skinner for the value of $-(E-e)$. In the present state of our information we are not entitled to make any assumption whatever on this question.

On page 277 Mr. Skinner gives a curve showing the behaviour of a Clark cell when continuously short-circuited so as to yield about ·01 ampere. The drop of P.D. is shown in this curve to increase continuously. From this it appears to be inferred (conclusion "*b*", page 278) that "the electromotive force of polarization slowly increases when the current is maintained;" and further on (page 279) Mr. Skinner says:—"In the experiments of Threlfall the sign of the term depending on time was found to be negative. In some of my earlier experiments it appeared to be negative, but this was traced to irregularity in the working of the compensator; and the effect has always been positive since the Clark cells have been used in the place of the Leclanché."

Now Mr. Pollock and I specially guarded ourselves in the paper referred to from any statement whatever as to the "electromotive force of polarization," having the fear of Lord Rayleigh and Professor Ayrton very properly before our eyes. Secondly, we fortunately have all our notes intact, and find that we kept a much better watch on the compensator than Mr. Skinner appears to have done; and there is no doubt whatever that, in the case we examined, the P.D. drop diminished with time, and this was to be explained neither by change of compensator nor by heating of short-circuiting resistance. We cannot ask the Editors to afford space for the voluminous numerical evidence to exhibit this rather unimportant fact; but we satisfied ourselves on this point in 1888, and since Mr. Skinner's paper appeared have gone into the matter again and find it to be as we stated in our paper. As a matter of fact our cells were not made up quite in the same way as Mr. Skinner's, and the zincs were wrapped in parchment-paper, the resistance of which may, not improbably, have varied considerably. In instituting his comparison Mr. Skinner apparently overlooked this point, and this leads me to think that he did not refer to our paper very carefully, though probably as carefully as it deserved. We are the more inclined to this view from the statement appearing in §8, "Conclusion," page 278, that "From the magnitudes of the quantities found in these experiments, it follows that small currents of approximately known value can be obtained by the use of large Clark cells of small internal resistance, which may be neglected in comparison with the large external resistance." Seeing that the primary object of our work was to discover whether such a proposition is true or not, that the greater part of our paper is taken up by a discussion as to the limits within which this proposition is true, that our results (much more numerous than Mr. Skinner's) are illustrated by two sheets of curves (plates xii. & xiii.), and, finally, that a method of determining high specific resistances based on this property of Clark cells has been in use almost daily in our laboratory since the paper was written in 1888, and was described by us (Phil. Mag. 1889, vol. xxviii. p. 470)—considering all this, I say that Mr. Skinner's unconditioned statement of his conclusion appears to me to be somewhat inadequate.

There is yet another point. On page 273, and referring to the measurement of the resistance of his cells, Mr. Skinner says:—"However, following Mr. Fitzpatrick's method, tests were specially made for polarization by varying the ratio of the arms and by varying the speed of the commutator." So far as varying the speed of the commutator goes, this method was described to all intents and purposes by Kohlrausch in Pogg. *Ann.*, *Jubelband*, p. 290, in Wiedemann's *Electricität*, vol. i. p. 476, and, I think, in Professor Chrystal's article in the *Encyclopædia Britannica*. It is therefore a mistake to ascribe it to Mr. Fitzpatrick.

R. THRELFALL.

Sydney, December 30, 1894.

XXVIII. *Value of the Magnetic Permeability for Rapid Electrical Oscillations.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,

THERE have been various estimations of the above quantity, but the results resting upon experimental data are few. A late paper by Ignaz Klemenčič in Wied. *Ann. der Physik und Chemie*, No. 12, 1894, contains the following values of the permeability in case of oscillations of 1,000,000 per second:—

Soft iron . . . . . $\mu=118$,

Steel . . . . . . $\mu=106$ to 115.

In a paper in the Philosophical Magazine for November 1894, on "Wave-Lengths of Electricity on Iron Wires," I obtained as a bye-result the average approximate value

$$\mu=385.$$

A recalculation of this value, however, shows an arithmetical error, which multiplies the value by 4, so that the true approximate value yielded by the data is $\mu=96$, ranging between the values 107 and 83·5, the extremes of the three values. These are lower than the results given by Klemenčič, but in my experiments the rate of oscillation was much higher.

In this connexion it is interesting to note that Mr. Oliver Heaviside, in his 'Electrical Papers,' vol. i. p. 361, "Waves of Magnetic Force," remarks that μ is eminently variable, but that a fair average value is $\mu=100$. This assumption seems confirmed both from Klemenčič's results and my own.

I am, Gentlemen,
Yours respectfully,
CHARLES E. ST. JOHN.

Berlin, Jan. 10, 1895.

XXIX. *On the Liquefaction of Gases.*
By Prof. J. DEWAR[*].

IN the Philosophical Magazine for last month Professor Olszewski has made serious allegations regarding my relations to his alleged discoveries. It is usually assumed that if a scientific man has a grievance on some question of priority, he speaks out boldly at or about the time when his discovery is being appropriated. It seems, however, that Professor Olszewski prefers to nurse his complaints for four years and then to bring them out simultaneously in two English scientific journals. The result, I am afraid, will be grievously disappointing. Personally I am delighted to see an English edition of Professor Olszewski's papers. There is, however, one serious omission which I trust the Editors of the Philosophical Magazine may remove before long. We want in this country a reprint of the splendid papers of the late Professor Wroblewski. Until this is done it will be impossible for the scientific public to decide on many of Professor Olszewski's claims for priority. Now let me turn to the Professor's treatment of myself. The following are the deliberate statements made by him in his paper "On the Liquefaction of Gases," Philosophical Magazine, February 1895:—

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[*] Communicated by the Author.

"But in his last experiments and lectures respecting the liquefaction of considerable quantities of oxygen and air and their employment as cooling agents, Professor Dewar has thought fit not to make any mention of my labours in the same field, which had been published several years before Professor Dewar went over them again. In the number for June 1890 of the *Bulletin International de l'Académie de Cracovie*, I have described an apparatus serving to liquefy a greater quantity of oxygen or air in a steel cylinder, from which it can be poured out into an open glass vessel, and used as a frigorific agent. It is entitled 'K. Olszewski. Transvasement de l'oxygène liquide ;' and a brief report on the subject is contained in the *Beiblätter* of Wiedemann, vol xv. p. 29, under the title 'K. Olszewski. Ueber das Giessen des flüssigen Sauerstoffs.' That my labours should have thus been passed over in silence is all the more astonishing, because as soon as the above-mentioned *Bulletin* was printed I sent a proof of it to Professor Dewar; I also forwarded him proofs of my other researches, knowing that they interest him.". . . .

"From this summary of researches, as well as of dates, it follows that the first apparatus serving to produce large quantities of the liquefied so-called permanent gases, with the solitary exception of hydrogen, was constructed by me. This apparatus can be enlarged at will by increasing its parts, but without changing anything in its construction, so that it might be used to obtain liquefied gases in factories should they at any time prove of practical utility. By means of this apparatus I obtained as large quantities of liquid gases as I wanted; and they were used for the first time on a large scale as cooling agents (for instance, in my attempts to liquefy hydrogen), or as an object of scientific researches (the absorption spectrum of liquefied oxygen, its coefficient of refraction, &c.).

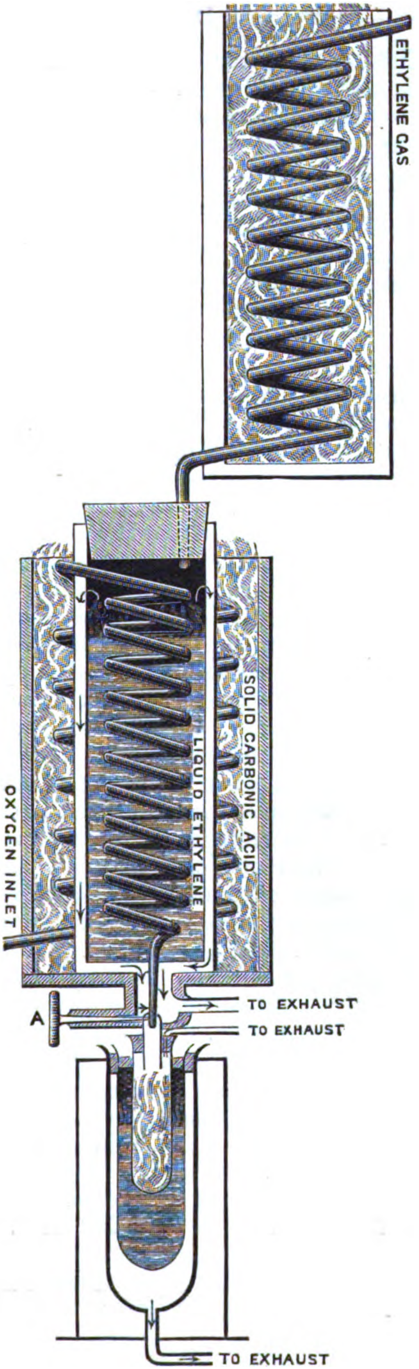
"The experiments of Professor Dewar are merely the repetition and confirmation of these researches, most of which were published several years before his corresponding investigations. His work is really original only as to the magnetic properties of liquid oxygen: that which is not borrowed from my researches is a development of ideas struck out by another —as, for instance, the experiments on electrical resistance at low temperatures, which were begun by Clausius, continued by Cailletet and Bouty, and brought ten years ago by my former fellow-worker, the late Professor Wroblewski, to the temperature of the freezing-point of nitrogen, then several degrees below the temperature attained in the experiments of

Messrs. Dewar and Fleming, who, it is true, extended their examination to various metals, alloys, and non-metals. But the execution of these labours meets with no difficulty; for the method of getting large quantities of liquefied gases is now generally known."

Let us see what Professor Olszewski said in that paper entitled "Transvasement de l'oxygène liquide," June 1890.

"A flask of wrought iron, 5 litres in capacity (such as is used to hold liquid carbon dioxide), containing oxygen under a pressure of 80 atm., is joined by a narrow copper tube to the upper end of a steel cylinder tested at a pressure of 200 atm. This cylinder, having a capacity of 30–100 cubic centim., according to the quantity of oxygen which we wish to liquefy at a time, is immersed in liquid ethylene, of which the temperature may easily be lowered to −140° C. by means of an air-pump. The lower end of the cylinder is joined by a narrow copper tube to a little stopcock, through which the oxygen, liquefied in the cylinder, can be poured down into an open glass vessel kept cool by the surrounding air."

In other words, replace the glass tube in my apparatus of 1884 by a small steel cylinder and attach to its lower end a narrow copper tube with a stopcock, and the Olszewski apparatus of 1890 would result. As a matter of fact Pictet had used the same principle in the year 1878, and to take credit for originality in repeating his device seems a little absurd. Now on the 11th of June, 1886, I delivered a lecture on "Recent Researches on Meteorites," and the report in the 'Proceedings of the Royal Institution' contains a sectional drawing of an apparatus (reproduced on the other page) solely constructed of copper, together with a valve for drawing off liquid oxygen, entirely different in type from the plan Olszewski adopted in 1890. I may mention that the plan of the apparatus was reproduced immediately after the delivery of the lecture both in England and America. The section is confined to the refrigerator, all the accessories of liquefied and compressed gas-bottles, compression and exhaust gauges, &c. having been omitted. From this plan of the refrigerator, any person so desiring could increase its capacity so as to work on a larger scale. The drawing shows the apparatus arranged for the special experiment of ejecting liquid oxygen into a vacuum-chamber, but it is clear the apparatus discharged more easily into an ordinary open vessel. *It is the form of apparatus that is in dispute, not the result of any particular experiment.* The special object for which it was in use in this lecture was to cool a piece of Meteorite before insertion into an Electric


ETHYLENE GAS
SOLID CARBONIC ACID
LIQUID ETHYLENE
OXYGEN INLET
A
TO EXHAUST
TO EXHAUST
TO EXHAUST

Furnace. The following extract from the lecture will explain how the subject was introduced :—

"Meteorites, no doubt, have an exceedingly low temperature before they enter the earth's atmosphere, and the question had been raised as to what chemical reactions could take place under such conditions. It resulted from Professor Dewar's investigations that at a temperature of about −130° C. liquid oxygen had no chemical action upon hydrogen, potassium, sodium, phosphorus, hydriodic acid, or sulphydric acid. It would appear, therefore, that as the absolute zero is approached even the strongest chemical affinities are inactive.

"The lecturer exhibited at work the apparatus by which he had recently succeeded in solidifying oxygen*. The apparatus is illustrated in the accompanying diagram [p. 301], where a copper tube is seen passing through a vessel kept constantly full of ether and solid carbonic acid ; ethylene is sent through this tube, and is liquefied by the intense cold ; it is then conveyed by the tube, through an indiarubber stopper, into the lower vessel ; the outer one is filled with ether and solid carbonic acid. A continuous copper tube about 45 feet long, conveying oxygen, passes through the outer vessel, and then through that containing the liquid ethylene ; the latter evaporates through the space between the two vessels, and thus intense cold is produced, whereby oxygen is liquefied in the tube to the extent occasionally of 22 cubic centimetres at one time. The temperature at which this is effected is about −130° C., at a pressure of 75 atmospheres, but less pressure will suffice. When the oxygen is known to be liquid, by means of a gauge near the oxygen inlet, the valve A is opened, and the liquid oxygen rushes into a vacuum in the central glass tube below ; some liquid ethylene at the bottom of the next tube, outwards, is also caused to evaporate into a vacuum at the same moment, and instantly some of the liquid oxygen in the central tube becomes solid, owing to the intense cold of the double evaporation. The outer glass vessel serves to keep moisture from settling on the sides of the ethylene tube. By means of the electric lantern and a lens, an image of this part of the apparatus was projected upon the screen, this being the first time that the experiment had been shown on a large scale in public.

"Performing this experiment the temperature reached was a little below 200° C., that is only 50° or 70° above the absolute zero of temperature, and in the experiment about 5 lbs. of solid ethylene were employed."

---

* The white material taken for solid oxygen in 1886 was due to gaseous impurity.

This I declare to be the first apparatus (Pictet's excluded) made wholly of metal, being an arrangement of copper coils in which liquid oxygen was made and decanted or transferred from the vessel in which it was liquefied to another by means of a valve and thereby rendered of use as a cooling agent. In support of this assertion I call as a witness Professor Charles Olszewski himself, who states in the Philosophical Magazine, February 1895, p. 189:—"In 1883, and for several years following, I liquefied the gases in a strong glass tube." There is no suggestion made that a steel cylinder and valve was used by Olszewski till the year 1890, whereas four years in advance I had used a much safer and better form of apparatus. Have I ever suggested that Professor Olszewski was anticipated, or attempted to raise any question of priority?

With regard to another case of priority that is claimed, I find that MM. Charles Olszewski and Auguste Witkowski, Membres Correspondants, présentent leur mémoire "Propriétés optiques de l'oxygène liquide," on the 3rd of October 1892, and, on referring to the paper, it is dated the 15th July 1892, and the following footnote is added:—

"Avant la publication de notre communication MM. Liveing et Dewar ont fait connaître (Phil. Mag. août 1892) les résultats de leurs recherches sur la réfraction des gaz liquéfiés."

But Professor Olszewski is not satisfied by a reference to published papers, he includes unpublished ones as well, in order to include the study of chemical action at low temperatures as having been originated by him. The following extracts from a well-known Continental Journal of what I had done in 1885 may induce him to produce his priority claim in a definite shape. I challenge him to produce any reference to antecedent work in this subject.

Extract from *Moniteur Scientifique*, vol. xv. (1885), p. 1134:—

"Sur les Solutions d'Ozone et l'action chimique de l'Oxygène liquide. Par Professor Dewar.

"Dans cette communication, le professeur a donné la description de l'appareil et de la méthode dont il s'est servi pour liquéfier les gaz tels que l'oxygène, et après avoir discuté les conditions requises pour le succès de la conversion des gaz dits permanents en liquides, il a rendu compte de plusieurs expériences faites avec l'oxygène liquide. A —130°

l'oxygène perd les caractères actifs possédés par cet élément dans l'état gazeux ; il est sans action sur le phosphore, le sodium, le potassium, l'hydrogène sulfuré solide et l'acide hydriodique solide. D'autres substances paraissent éprouver des changements semblables aux très basses températures. Ainsi l'éthylène liquide et le brome solide peuvent être mis en contact sans produire aucune action, tandis que l'éthylène gazeux et le brome liquide s'unissent directement aux températures ordinaires.

"Hautefeuille et Chapuis, en soumettant un mélange d'anhydride carbonique et d'ozone à une grande pression, ont obtenu un liquide bleu dont la couleur est dûe à l'ozone. Si l'air ozonisé passe dans du disulphide de carbone à $-100°$, le liquide prend une couleür bleue qui disparaît quand on laisse élèver la température, et, à un certain degré, une décomposition d'où résulte une production de soufre. Le meilleur dissolvant de l'ozone est un mélange de tétrafluoride de silicum et de pétrole de Russie. Ces solutions d'ozone sont sans action sur le mercure ou l'argent métalliques."

Prof. Olszewski says :—" The experiments of Prof. Dewar are merely the repetition and confirmation of these researches." Reviewing the work I have been engaged upon during the last few years, either by myself or in consort with Profs. Liveing or Fleming, the following subjects have been taken in hand and so far developed with regard to the properties of matter at low temperatures :—

Construction of Apparatus for the production of Liquid Air and other Gases in quantity—High Vacua—Vacuum Vessels for Storage and Manipulation of Liquid Gases—Cooling by Sponge of Liquid Air—Solid Air—Radiation at Low Temperatures—Thermal Transparency—Refractive Indices—Spectroscopy—Electric Conductivity—Thermo-Electric Properties—Latent and Specific Heats—Capillarity—Chemical Action—Magnetic Properties—Breaking-Stress of Metals—Solid Matter and Argon in Liquid Air—Phosphorescence and Photographic Action—Liquefaction of Hydrogen, &c. With the exception of the determination of the refractive indices of liquid oxygen my work has had nothing in common with that of Prof. Olszewski.

Now Prof. Olszewski says he has anticipated all this pioneering work. On referring to his list of papers given in the Philosophical Magazine for last month, I find that since the year 1890 he has confined his attention to the refractive indices of liquid oxygen and an attempt to corroborate Wroblewski's determination of the critical constants of hydrogen. No one knows better than myself that the fringe of the subject only is touched. When the investigator has the means of examining the general properties of matter under new conditions, surely in our time he does not claim originality for the selection of the order in which he attacks the many problems ready to hand? The fact is the claims set forward by Prof. Olszewski are fantastic and unfounded.

Professor Olszewski has done good work in the determination of the pressure and temperature relations of the liquid gases, but in future it is to be hoped he will modify his claim for general priority in everything relating to Low Temperature Research.

Royal Institution, 14th Feb. 1895.

XXX. *Notices respecting New Books.*

Select Methods in Chemical Analysis (chiefly Inorganic). By WILLIAM CROOKES, *F.R.S. &c.* 3rd edition, rewritten and enlarged. (London: Longmans, Green, & Co., 1894.)

THE subject of chemical analysis is capable of being regarded from two points of view—first as a means of training students in exactness of work, neatness, cleanliness, carefulness, and so forth, and in the next place as a practical branch of science which the working chemist is constantly obliged to resort to in order to ascertain the composition of some kind of matter. This book by Mr. Crookes, which has now reached its third edition, appeals to the latter rather than to the former class of readers. It has in fact from the time of its appearance occupied a unique position among kindred works, and the new edition will be welcomed by working chemists with the same gratitude that its predecessors were received with when the author first enriched our chemical literature with a compilation of such real practical value. In speaking of the work as a compilation, we have no desire to detract from its merits. To expect the author of a book on chemical analysis to originate all the processes described would be simply absurd, but, although confessedly a compilation, there is one feature that lifts the present work quite above the level of such productions. A quotation from the preface will explain our statement:—

"The author has merely given such methods as have been proved in his own laboratory. Others—possibly no less efficient—have been passed over because he cannot vouch personally for their value. A main object has been to bring into notice a number of little-known expedients and precautions which prevent mistakes, insure accuracy, or economise time."

The user of this book therefore may rest assured that all the processes described have received the approval of one of the most skilful masters of chemical analysis in this country.

Taking it for granted that the work has, by virtue of its merits, established for itself such a position that any further commendation on the part of a reviewer would be superfluous, we have only to point out now wherein the present edition differs from the former one which was published eight years ago. In order to justify the title of the work and to keep to its spirit, many of the older and now well-known methods of estimation have been omitted. In fact, these methods have passed from the "select" stage, and, having undergone the test of experience, are now embodied in all works on analysis, so that the working chemist may be assumed to know all about them or (what comes to the same thing) where to find them when wanted. Other processes have, we are told, been left out for the opposite reason—because they have not stood the ordeal of experience, but have been supplanted by better ones. The ordinary volumetric processes have also been omitted because there are special works, such as that by Sutton, dealing with this subject. Only in certain cases are titration methods described, and then because of their selectness. For a similar reason the ordinary pyrological methods of analysis no longer find place in the volume, but the reader is referred to special treatises on assaying, of which there are several well-known ones.

The effect of all this expurgation, however, has not been to diminish the size of the book, because a large amount of new matter has been added, partly in the form of new processes which have been discovered since the last edition, but more particularly in the form of descriptions of the electrolytic methods of estimating metals, which have been so thoroughly worked out of late by Dr. Classen. This part of the work, which will be found particularly useful to English chemists, confessedly owes its origin to Classen's book, many of the illustrations of apparatus having been taken from this source. Altogether the volume extends with its index to 718 pages, and is divided into sixteen chapters. Of these the first deals with the alkaline metals; the second with the alkaline earths; the third with the rare earths (on which the author is the chief living authority); the fourth with chromium, vanadium, uranium, tungsten, and molybdenum; the fifth with zinc, aluminium, gallium, and iron; the sixth with manganese, nickel, and cobalt; the seventh with silver, mercury, and copper; the eighth with cadmium, gallium, lead, thallium, indium, bismuth; the ninth with antimony, tin, arsenic, selenium, and tellurium; the tenth with gold and the platinum metals; the eleventh with sulphur, phosphorus, and nitrogen; the twelfth with the halogens and cyanogen; and the thirteenth with carbon, silicon, and boron. In the fourteenth chapter the electrolytic method and certain special methods of gas-analysis are described. Chapter xv. is devoted to certain miscellaneous processes and what in laboratory terms would be called "practical dodges." The concluding chapter contains sets of useful tables.

The general scope of the work will be inferred from the foregoing account of its contents. The classification of the elements may appear somewhat arbitrary, but there are good analytical reasons for adopting this arrangement. The details of description have all the lucidity and exactness which we are accustomed to find in Mr. Crookes' writings. Although nearly a quarter of a century has elapsed since the appearance of the first edition, there is no falling off in power of treatment anywhere manifest in the pages of the present volume, the completion of which is a matter of congratulation both for the veteran author and the chemical world.

A Few Chapters in Astronomy. By CLAUDIUS KENNEDY, *M.A.* (Crown 8vo, 150 pp., 40 illustrations. London: Taylor & Francis, 1894.)

THE idea of this book is a very good one. Its object is to elucidate more fully certain points which are merely touched on or only imperfectly explained in works on Astronomy and Mechanics. In the first Chapter we have an explanation of an optical illusion which is frequently noticed, even by casual observers, but of which the reason is not generally understood. This is the fact that a line drawn at right angles to a line joining the horns of the crescent Moon does not seem to pass through the Sun, as of course it really does, but some distance above it. A similar illusion is seen in the apparent downward curvature of meteor-tracks, and the apparent curvature (in some cases) of a comet's tail when very long, as in the Great Comet of 1882. The second Chapter deals with the effect of the Earth's rotation on moving bodies, such as bodies falling from a height, the flight of migrating birds, &c. The third Chapter explains the effect of the Earth's rotation on projectiles. The subject is very fully worked out, and in a very interesting manner. In Chapter IV. an explanation is given of the principle of Foucault's pendulum, a subject which is not sufficiently explained in ordinary text-books on Astronomy, especially with reference to places between the equator and the poles. Chapter V. contains an investigation of the position of high tide considered on dynamical principles—a subject which is very imperfectly dealt with in most works on Astronomy. In Chapter VI. we have a description of various forms of the "Horizontal Pendulum," an instrument which is not generally known, and which was devised for the purpose of detecting by direct observation the Moon's differential tidal force. Although sound in theory, this instrument does not seem to be capable of giving any definite results in practice; for, as Mr. Kennedy says, "in most cases, at least, a gentle breeze pressing on the side of a house would make the whole basement floor tilt to leeward through an angle considerably greater than the greatest change in the vertical by the Moon's tidal force."

Chapters VII. and VIII. deal with the Moon's Variation and

Parallactic Equality, subjects which are not sufficiently developed in Astronomical treatises. The author clearly explains some points in these lunar irregularities which the student may find a difficulty in thoroughly understanding, and clears up some *apparent* paradoxes with which the subject is beset.

On the whole, this little work will be found of great assistance to students of mathematical astronomy, and we can strongly recommend it to their attention. J. E. GORE.

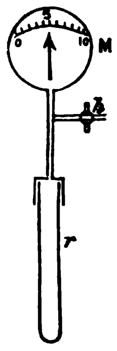
XXXI. *Intelligence and Miscellaneous Articles.*

AN EXPERIMENT WITH SOLID CARBONIC ACID.

BY PROF. K. PRYTZ.

INCITED by the interesting account by Prof. Bleekrode (Phil. Mag. xxxviii. pp. 81–89, 1894) of his experiments with solid carbonic acid, I wish to describe an experiment which I have made. A quantity of solid carbonic acid being compressed in a wooden cylinder, I cut the block of the substance in pieces small enough to be put into a stout glass tube *r* 1·5 centim. wide. When the tube was filled with the pieces of carbonic acid, it was connected with a manometer M, the cock *h* being open. On closing the cock the index of the manometer rises slowly until the pressure is as much as 5 atm. The index then stands completely still for a tolerably long time; at the same time we see pieces of carbonic acid sink down on melting: only when the whole is melted, and consequently fills the bottom of the tube, does the index suddenly rise again, and now *much faster than before.*

When the index has reached 10 atm. the cock is opened a little: the melted carbonic acid then evaporates quickly, the pressure diminishes, the index goes back to 5 atm.: there it suddenly stops again, and is stationary until the carbonic acid is again solid, whereupon it slowly goes back to 1 atm.



The experiment is very instructive. It shows better than any other that I know of the fixity and the identity of the melting and solidifying points: it shows that solid carbonic acid only melts under pressure, and it indicates the great difference between the solid and the liquid carbonic acid in respect of conductivity for heat.

I usually place the glass tube in water; the transparent ice crust then formed shows the cold inside the tube.

The Physical Laboratory of the
Polytechnical School at Copenhagen.

THE

LONDON, EDINBURGH, AND DUBLIN

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[FIFTH SERIES.]

APRIL 1895.

XXXII. *On the Passage of an Oscillator Wave-train through a Plate of Conducting Dielectric.*

By GEORGE UDNY YULE, *Demonstrator in Applied Mathematics, University College, London.*

I. Introduction.
II. The Phenomena at the First Surface of the Plate.
III. The Phenomena at the Second Surface of the Plate.
IV. The Intensity of the Transmitted Ray.
V. The Intensity of the Reflected Ray.
VI. Discussion of an Experimental Case and a Correction.
VII. The Numerical Value of some of the previous Results.
Synopsis of Symbols.

I. *Introduction.*

THE problem treated in these pages was suggested by the following experimental results, for a fuller account of which I may refer to a previous paper[†].

A series of wave-trains generated by an oscillator O were allowed to propagate themselves along a double-wire circuit LL′ about 100 metres in length. At the middle of the circuit the wires were run through a jar containing a certain depth AB of distilled water, alcohol, or a very dilute electrolyte.

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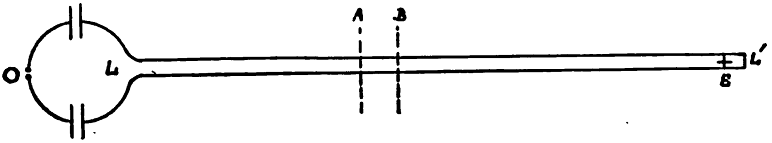
[*] Communicated by the Physical Society: read January 11, 1895.

[†] Phil. Mag. vol. xxxvi. p. 531, Dec. 1893. Prelim. Paper in the Proc. Roy. Soc. vol. liv. p. 96. A sketch of an approximate theory was given in the Phil. Mag. paper, but several assumptions there made were unjustifiable.

The intensity of the ray transmitted by this slightly absorbent layer was determined by an electrometer E placed at a quarter wave-length (2·25 metres) from the closed end of the circuit.

Fig. 1.



This intensity varied periodically with the thickness of the layer, as in the analogous case of a ray of light and a "thin plate."

The layer AB was what Boltzmann has termed a "conducting dielectric," *i. e.* both its conducting and dielectric properties were of importance. The theory of a non-conducting plate is much simpler: a problem equivalent to it has recently been treated by Dr. E. H. Barton *, to whose work I shall have several occasions to refer. In the more complex problem I have assumed, we have simply a plane-fronted damped wave-train travelling through an insulating medium and falling at normal incidence on an infinite slab of conducting dielectric. The magnetic permeability of both the plate and the surrounding medium are taken as unity.

The theoretical transmission-curve obtained on these assumptions does not agree well with the experimental one, the divergence being the same in sign and order of magnitude as that noticed by Dr. Barton in his case. We have in fact idealized the experimental facts too far in endeavouring to simplify the analysis: the electrolyte was not at all infinite in extent, and at least one important correction is obviously necessary (section VI.). The experiments can only be regarded as a very rough illustration of the problem, and as giving the *raison d'être* of this paper.

The general results obtained seem to be of considerable interest. The intensities of the reflected rays, the phase-changes, and so on, for damped wave-trains reflected from such a plate differ from those for steady rays in some cases very considerably.

For convenience and brevity, the surrounding medium is hereinafter generally referred to as "the dielectric," and the conducting slab as "the plate" or "electrolyte."

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* Preliminary Paper, Proc. Roy. Soc. vol. liv. p. 85; more fully in Thesis for the D.Sc. London, 1894, or Wied. *Ann.* vol. liii. p. 513, 1894. Final paper, Proc. Roy. Soc., read April 1893 (not yet published).

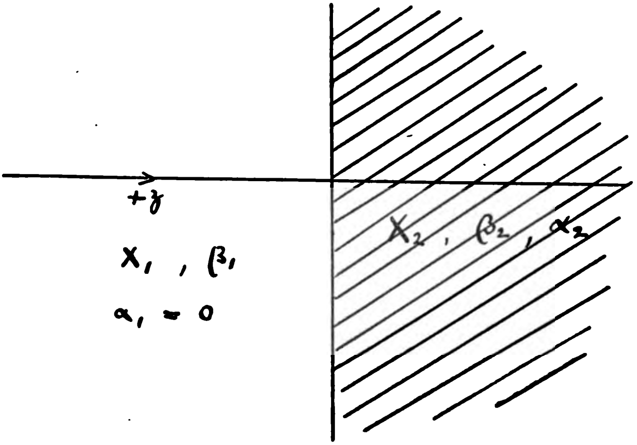
II. *The Phenomena at the First Surface of the Plate.*

In this section we will deal with the phenomena occurring at the first surface of the "electrolyte" only.

The direction of propagation of the ray is chosen as the positive direction of the axis of z and the origin is taken indefinitely close to the interface.

The suffix 1 always refers to the dielectric and the suffix 2 to the plate.

Fig. 2.



Let X_1 be the electric force in the dielectric and X_2 that in the plate. Under the limitations we have set ourselves—plane waves and non-conducting dielectric—Maxwell's equations assume the simple forms

$$\beta_1 \frac{d^2X_1}{dt^2} = \frac{d^2X_1}{dz^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\left(\alpha_2+\beta_2\frac{d}{dt}\right)\frac{dX_2}{dt} = \frac{d^2X_2}{dz^2}, \quad . \quad . \quad . \quad . \quad (2)$$

where we have abbreviated Maxwell's notation by putting

$$\beta_1=\mu_1\kappa_1, \quad \beta_2=\mu_2\kappa_2, \quad \alpha_2=4\pi\mu_2C_2, \quad . \quad . \quad (3)$$

μ_2 being the magnetic permeability of the plate, κ_2 its dielectric constant, C_2 its conductivity; μ_1 κ_1 are the same constants referring to the dielectric, C_1 being zero. As already stated, we will only take the case of both media being non-magnetic, or

$$\mu_2 = \mu_1 = 1.$$

As a solution of equations (1) and (2) we select

$$\left.\begin{aligned} X_1 &= A_1 e^{p(t - \sqrt{\beta_1} z)} + A_1' e^{p(t - \sqrt{\beta_1} z)} \\ X_2 &= B_2 e^{p(t - qz)} \end{aligned}\right\} \quad . \quad . \quad (4)$$

where t must be not less than zero. p is either wholly imaginary or complex according as the incident ray is steady or damped: q is as yet undetermined; A_1 is the amplitude of the incident wave-train, A_1' of the reflected wave-train, and B_2 of the transmitted wave-train.

Inserting the value of X_2 given in (4) in equation (2), and carrying out the differentiation, we get

$$q = \sqrt{\beta_2}\left(1 + \frac{\alpha_2}{\beta_2 p}\right)^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

so q is also partly imaginary.

To determine $\frac{A_1'}{A_1}$ and $\frac{B_2}{A_1}$ we require another pair of equations. These will be given us by the interface conditions: the conditions namely, that there must be no discontinuous jump in the values of either the tangential electric force or the tangential magnetic force, at any time, in passing from the dielectric to the electrolyte. That is, we must have

$$\left.\begin{aligned} X_1 &= X_2, \\ \frac{dX_1}{dz} &= \frac{dX_2}{dz}, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where

$$z = 0, \quad t = \text{anything}.$$

Inserting the values of X_1 and X_2 in (6) we get, putting $z = 0$,

$$\left.\begin{aligned} A_1 + A_1' &= B_2, \\ p\sqrt{\beta_1}\,(-A_1 + A_1') &= -pqB_2; \end{aligned}\right\} \quad . \quad . \quad . \quad (7)$$

and solving these two equations for $\frac{A_1'}{A_1}$, $\frac{B_2}{A_1}$,

$$\frac{A_1'}{A_1} = -\frac{\dfrac{q}{\sqrt{\beta_1}} - 1}{\dfrac{q}{\sqrt{\beta_1}} + 1},$$

$$\frac{B_2}{A_1} = \frac{2\sqrt{\beta_1}}{\sqrt{\beta_1} + q}.$$

If we write for brevity

$$\lambda=\frac{\sqrt{\beta_1}}{q},$$

$$\left.\begin{aligned}\frac{A_1'}{A_1}&=-\frac{1-\lambda}{1+\lambda},\\ \frac{B_2}{A_1}&=\frac{2\lambda}{1+\lambda},\end{aligned}\right\} \quad \ldots\ldots \quad (8)$$

λ contains q, which is partly imaginary; so we must separate the real and imaginary quantities and rationalize. Let p_1 be the real part of p, and p_2 the imaginary part, so that

$$p=-p_1+p_2 i,$$

and let us write

$$\left.\begin{aligned}p_1&=\eta\cos\chi,\\ p_2&=\eta\sin\chi.\end{aligned}\right\} \quad \ldots\ldots \quad (9)$$

In this notation then

$$\left.\begin{aligned}p&=-\eta e^{-i\chi},\\ \text{period}&=\frac{2\pi}{p_2},\\ \text{logarithmic decrement}&=\frac{2\pi p_1}{p_2};\end{aligned}\right\}$$

and using the value of q in (5),

$$\lambda=\sqrt{\frac{\beta_1}{\beta_2}}\frac{1}{\left(1-\frac{\alpha_2}{\eta\beta_2}e^{i\chi}\right)^{\frac{1}{2}}}.$$

The denominator of this expression is

$$\left(1-\frac{\alpha_2}{\eta\beta_2}\cos\chi-i\frac{\alpha_2}{\eta\beta_2}\sin\chi\right)^{\frac{1}{2}},$$

so if we put

$$\left.\begin{aligned}\rho\cos\theta&=1-\frac{\alpha_2}{\eta\beta_2}\cos\chi\\ \rho\sin\theta&=\frac{\alpha_2}{\eta\beta_2}\sin\chi\end{aligned}\right\}, \quad \ldots \quad (10)$$

or

$$\rho=\left[1-\frac{\alpha_2}{p_2\beta_2}\sin 2\chi+\left(\frac{\alpha_2}{p_2\beta_2}\sin\chi\right)^2\right]^{\frac{1}{2}}$$

$$\tan\theta=\frac{\frac{\alpha_2}{p_2\beta_2}\sin^2\chi}{1-\frac{1}{2}\frac{\alpha_2}{p_2\beta_2}\sin 2\chi},$$

the denominator becomes $\rho e^{-\frac{i\theta}{2}}$. Writing

$$r=\sqrt{\frac{\beta_1}{\beta_2}}\,\frac{1}{\sqrt{\rho}}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (11)$$

as a further abbreviation we have

$$\lambda=re^{\frac{i\theta}{2}}.$$

We can now proceed to rationalize the values of $\frac{A_1'}{A_1}$ and $\frac{B_2}{A_1}$ given in (8). Inserting our value of λ,

$$\frac{A_1'}{A_1}=-\frac{1-re^{\frac{i\theta}{2}}}{1+re^{\frac{i\theta}{2}}}=-\frac{1-r\cos\frac{\theta}{2}-ir\sin\frac{\theta}{2}}{1+r\cos\frac{\theta}{2}+ir\sin\frac{\theta}{2}}.$$

Multiplying numerator and denominator by

$$1+r\cos\frac{\theta}{2}-ir\sin\frac{\theta}{2},$$

this becomes

$$-\frac{1-r^2-2ir\sin\frac{\theta}{2}}{1+r^2+2r\cos\frac{\theta}{2}},$$

and multiplying again by $1-r^2+2ir\sin\frac{\theta}{2}$,

$$\frac{A_1'}{A_1}=-\frac{1+r^4-2r^2\cos\theta}{\left(1+r^2+2r\cos\frac{\theta}{2}\right)\left(1-r^2+2ir\sin\frac{\theta}{2}\right)}.$$

If then

$$\tan\psi=\frac{2r\sin\frac{\theta}{2}}{1-r^2}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

we have finally

$$\frac{A_1'}{A_1}=-\frac{(1+r^4-2r^2\cos\theta)^{\frac{1}{2}}}{1+r^2+2r\cos\frac{\theta}{2}}e^{-i\psi};$$

that is, the ray reflected from the first surface of the plate undergoes a phase-change of $(-\psi)$, the reduction factor or ratio of the *amplitude* of the reflected to that of the incident ray being

$$b=-\frac{(1+r^4-2r^2\cos\theta)^{\frac{1}{2}}}{1+r^2+2r\cos\frac{\theta}{2}}. \quad . \quad . \quad . \quad . \quad . \qquad (13)$$

b is a function of the period and damping of the wave-train as well as of the properties of the reflector. If the wave-train be not damped, we have

$$\left.\begin{aligned} \chi &= 90^\circ, \\ \rho &= \sqrt{1+\left(\frac{\alpha_2}{p_2\beta_2}\right)^2}, \\ \cos\theta &= \frac{1}{\rho}, \end{aligned}\right\} \quad . \quad . \quad . \quad (14)$$

so the expression for b remains unaltered in form, b being still a function of the period.

But if the conductivity of the electrolyte or α_2 be zero, the angle θ becomes likewise zero, ρ is unity, and we get the ordinary value for b, namely,

$$b = \frac{1-\sqrt{\frac{\beta_1}{\beta_2}}}{1+\sqrt{\frac{\beta_1}{\beta_2}}}, \quad . \quad . \quad . \quad . \quad . \quad (15)$$

the period and damping of the incident ray having vanished from the expression.

The phase-change ψ is zero for either a perfect insulator or a perfect conductor; θ becoming indefinitely small in the first case, and r in the second.

The refracted wave is dealt with in exactly the same manner. Taking the value of $\frac{B_2}{A_1}$ from (8), and substituting in it the value of λ from (11) we have

$$\frac{B_2}{A_1} = \frac{2\lambda}{\lambda+1} = \frac{2re^{\frac{i\theta}{2}}}{1+re^{\frac{i\theta}{2}}}$$

$$= \frac{2re^{\frac{i\theta}{2}}\left(1+r\cos\frac{\theta}{2}-ri\sin\frac{\theta}{2}\right)}{1+r^2+2r\cos\frac{\theta}{2}}.$$

If we write

$$\tan\psi' = \frac{r\sin\frac{\theta}{2}}{1+r\cos\frac{\theta}{2}}, \quad . \quad . \quad . \quad . \quad (16)$$

then
$$\frac{B_2}{A_1} = \frac{2r}{\sqrt{1+r^2+2r\cos\frac{\theta}{2}}}e^{i(\theta/2-\psi}.$$

Thus for the transmitted ray at the dielectric-electrolyte surface, the change of phase is $\frac{\theta}{2}-\psi'$, and the ratio of its amplitude to that of the incident ray or c is

$$c=\frac{2r}{\sqrt{1+r^2+2r\cos\frac{\theta}{2}}}. \quad . \quad . \quad . \quad . \quad (17)$$

c, like b, is a function of the period and damping of the incident ray; like b it remains a function of the period even for an undamped ray; and like b it becomes a function of the dielectric constants only, if the "electrolyte" be a perfect insulator, the expression in (17) becoming

$$c=\frac{2\sqrt{\frac{\beta_1}{\beta_2}}}{1+\sqrt{\frac{\beta_1}{\beta_2}}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (17a).$$

We have now sufficient data to determine the speed of propagation and wave-length in the electrolyte, before going on to deal with the reflexions and refractions at the second surface. Referring back to equation (4) for X_2, and substituting the values we have determined for B_2, p, and q, we have

$$X_2=cA_1e^{i(\theta/2-\psi')}e^{(-p_1+ip_2)t}e^{\eta\sqrt{\beta_2\rho}\{\cos(\chi+\theta/2)-i\sin(\chi+\theta/2)\}z},$$

or retaining only the real terms

$$X_2=cA_1e^{-p_1t+\eta\sqrt{\beta_2\rho}\cos\left(\chi+\frac{\theta}{2}\right)z}\cos\left\{p_2t-\eta\sqrt{\beta_2\rho}\sin\left(\chi+\frac{\theta}{2}\right)z\right.$$
$$\left.+\frac{\theta}{2}-\psi'\right\}. \quad . \quad . \quad . \quad (18)$$

Hence the speed of the wave in the electrolyte is

$$V_2=\frac{p_2}{\eta\sqrt{\beta_2\rho}\sin\left(\chi+\frac{\theta}{2}\right)}=\frac{\sin\chi}{\sqrt{\beta_2\rho}\sin\left(\chi+\frac{\theta}{2}\right)}, \quad . \quad (19)$$

and the wave-length

$$\lambda_2=\frac{2\pi}{\eta\sqrt{\beta_2\rho}\sin\left(\chi+\frac{\theta}{2}\right)}. \quad . \quad . \quad . \quad (20)$$

But for the incident wave-train

$$\lambda_1 = \frac{2\pi}{p_2\sqrt{\beta_1}},$$

therefore

$$\frac{\lambda_2}{\lambda_1} = \sqrt{\frac{\beta_1}{\beta_2}}\,\frac{p_2}{\eta\sqrt{\rho}\sin\left(\chi+\frac{\theta}{2}\right)}$$

$$= \sqrt{\frac{\beta_1}{\beta_2}}\,\frac{\sin\chi}{\sqrt{\rho}\sin\left(\chi+\frac{\theta}{2}\right)} \quad . \quad . \quad . \quad . \quad (21)$$

ρ and θ being both functions of α_2 and of the period, and χ being a function of the rate of damping of the wave-train, $\frac{\lambda_2}{\lambda_1}$ is (like b and c and the phase-changes) a function of period, damping, and conductivity, except when the latter is zero: when we have simply

$$\frac{\lambda_2}{\lambda_1} = \sqrt{\frac{\beta_1}{\beta_2}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (21a)$$

III. *The Phenomena at the Second Surface of the Plate.*

We now proceed to the inverse case where the wave is passing from the electrolyte into the dielectric.

If X_2 represent as before the electric force in the electrolyte, and X_3 represent the electric force in the second dielectric, we may now write

$$X_2 = B_1\,e^{p(t-qz)} + B_1'e^{p(t+qz)}, \quad . \quad . \quad . \quad . \quad (22)$$

$$X_3 = A_3\,e^{p(t-\sqrt{\beta_1}z)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

the wave in the electrolyte consisting of a direct and a reflected train, and that in the dielectric of a direct train only.

Applying the interface conditions as in the last section, we get for $z=0$

$$B_1 + B_1' = A_3, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

$$\frac{dX_2}{dz} = \frac{dX_3}{dz}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Carrying out the differentiation of (25) and putting $z=0$,

$$-p\sqrt{\beta_1}A_3 = pq(-B_1 + B_1'),$$

or

$$B_1 - B_1' = A_3\,\frac{\sqrt{\beta_1}}{q} = A_3\lambda. \quad . \quad . \quad . \quad (26)$$

Solving for $\frac{B_1'}{B_1}$ and $\frac{A_3}{B_1}$ from (24) and (26) we get

$$\left.\begin{aligned} \frac{A_3}{B_1} &= \frac{2}{1+\lambda} \\ \frac{B_1'}{B_1} &= \frac{1-\lambda}{1+\lambda} \end{aligned}\right\} \quad \ldots\ldots \quad (27)$$

Using our previous notation of

$$\lambda = re^{\frac{i\theta}{2}}$$

and rationalizing, we obtain finally for the transmitted ray

$$\frac{A_3}{B_1} = \frac{2}{\sqrt{1+r^2+2r\cos\frac{\theta}{2}}}e^{-i\psi'},$$

so that the phase-change for the wave emerging from the electrolyte is $-\psi'$ (equation 16), and the reduction factor

$$f = \frac{2}{\sqrt{1+r^2+2r\cos\frac{\theta}{2}}} \quad \ldots\ldots \quad (28)$$

The expression for $\frac{B_1'}{B_1}$ in (27) is the same as that for $\frac{A_1'}{A_1}$ in (8) except for the reversal of sign, so the phase-change at the second surface of the electrolyte is the same $(-\psi)$ in magnitude and sign as at the first surface, and the reduction factor

$$e = -b. \quad \ldots\ldots \quad (29)$$

If the electrolyte be replaced by an insulator, f takes the ordinary form

$$f = \frac{2}{1+\sqrt{\frac{\beta_1}{\beta_2}}}, \quad \ldots\ldots \quad (30)$$

and the relation

$$cf = 1 - b^2$$

holds. In the general case there is no such relation.

IV. *The Intensity of the Transmitted Ray.*

We have now all the data necessary for treating the general case of a wave-train passing through a plate of finite thickness. We will first take the incident wave-train and follow its history in detail to obtain the expressions for the rays emergent after 0, 2, 4, . . . &c. internal reflexions. Let the incident wave-train be given by

$$\mathrm{A}\, e^{p(t-\sqrt{\beta_1}z)}$$

from the time $t=0$ onwards, p being a complex quantity as defined by (9). Passing through the first surface and reaching the second the wave becomes (d being the thickness of the electrolyte)

$$\mathrm{A}\, c\, e^{p(t-qd)}\, e^{i(\theta/2-\psi')},$$

and emerges in the form

$$\mathrm{A} cf e^{-pqd}\, e^{i(\theta/2-2\psi')}\, e^{p(t-\sqrt{\beta_1}z)}. \quad . \quad . \quad . \qquad \text{(I.)}$$

If we take the instant at which the incident wave first strikes the plate as the origin of time, the wave-train (I.) begins to emerge at time

$$t_2 = \frac{d\,.\,\eta\,.\,\sqrt{\beta_2 \rho}\,.\sin\left(\chi+\frac{\theta}{2}\right)}{p_2}, \quad . \quad . \quad . \qquad (31)$$

by equation (19).

The wave reflected from the second surface at the time that (I.) emerges is

$$-\mathrm{A}\,.\,bc\,e^{-pqd}\,e^{p(t+qz)}\,e^{i(\theta/2-\psi'-\psi)},$$

which becomes on reflexion at the first surface

$$\mathrm{A}\,.\,b^2 c\,e^{-2pqd}\,e^{p(t-qz)}\,e^{i(\theta/2-\psi'-\psi)},$$

and emerges from the second surface at time $3t_2$ as

$$\mathrm{A} b^2 cf e^{-3pqd} e^{p(t-\sqrt{\beta_1}z)} e^{i(\theta/2-2\psi'-2\psi)}. \quad . \quad . \quad . \qquad \text{(II.)}$$

This is the second emergent ray, or the ray emerging after two internal reflexions. The third emergent ray will be

$$\mathrm{A} b^4 cf e^{-5pqd}\, e^{i(\theta/2-2\psi'-4\psi)} e^{p(t-\sqrt{\beta_1}z)}, \quad . \quad . \quad . \qquad \text{(III.)}$$

emerging at time $5t_2$; and so on for the others. The $(n+1)$th emergent ray, or the ray emerging after $2n$ internal reflexions, is

$$\mathrm{A} b^{2n} cf e^{-(2n+1)pqd} e^{i(\theta|2-2\psi'-2n\psi)}\, e^{p(t-\sqrt{\beta_1}z)},$$

which emerges at time $(2n+1)t_2$. Remembering that

$$p=-p_1+p_2i=\eta(-\cos\chi+i\sin\chi),$$

$$q=\frac{\sqrt{\beta_1}}{\lambda}=\sqrt{\beta_2\rho}\left(\cos\frac{\theta}{2}-i\sin\frac{\theta}{2}\right),$$

this becomes

$$\mathrm{A}cfb^{2n}e^{(2n+1)\kappa d}e^{-p_1t}e^{i[p_2t+\alpha-(2n+1)(p_2t_2+\psi)]}, \quad . \quad . \quad . \quad (32)$$

where we have written for brevity

$$\left.\begin{aligned}\eta\sqrt{\beta_2\rho}\cos\left(\frac{\theta}{2}+\chi\right)&=\kappa,\\ \frac{\theta}{2}-2\psi'+\psi&=\alpha.\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (33)$$

Finally, if we take the initial form of the wave-train to be given by the sine terms, we may write this ray emerging after $2n$ internal reflexions, y_n, as

$$y_n=\mathrm{A}\,.\,cf\,.\,b^{2n}e^{(2n+1)\kappa d}e^{-p_1t}\sin\left[p_2t+\alpha-\overline{2n+1}(p_2t_2+\psi)\right]. \quad (34)$$

However small ψ may be it should evidently be retained, as it may become of importance owing to the multiple reflexions.

The wave-train y_n emerges at time $\overline{2n+1}t_2$. From $\overline{2n+1}t_2$ to $\overline{2n+3}t_2$, y_0 to y_n inclusive are the only wave-trains in existence. The total energy of any wave-train varies as the time-integral of the square of the "displacement"

$$(y), \text{ or } (y_0+y_1+y_2+\ldots+y_n).$$

We will call this time-integral the *intensity* of the wave-train (or set of wave-trains forming the ray), though we are not using intensity in its ordinary sense.

To get the intensity of the ray transmitted through the plate, we shall then have to sum up a series of integrals partly of squares $(y_0^2, y_1^2, \ldots y_n^2)$ and partly of products $(2y_m y_n$ &c.$)$: that is to say, if we call the intensity of the transmitted ray I_t,

$$\mathrm{I}_t=\mathop{\mathrm{S}}_{n=0}^{n=\infty}\int_{\overline{2n+1}t_2}^{\infty}y_n^2\,dt+2\mathop{\mathrm{S}}_{m=0}^{m=n-1}\mathop{\mathrm{S}}_{n=1}^{n=\infty}\int_{\overline{2n+1}t_2}^{\infty}y_m\,y_n\,dt. \quad . \quad . \quad (35)$$

In the experimental case the deflexions of the electrometer at E, fig. 1, are proportional to I_t.

We have now to get out the integrals in (35) and sum them. We will first multiply out the product $y_m y_n$ from the expression for y_n given in (34). This can then be integrated, and the integral of y_n^2 obtained by putting $m=n$.

Writing, for brevity,

$$p_2t_2 + \psi = \delta, \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

$$y_m y_n = \mathrm{A}^2c^2f^2 b^{2(n+m)}e^{-2p_1t}e^{2(m+n+1)\kappa d}$$
$$\times \sin(p_2t+\alpha-\overline{2n+1}\delta)\sin(p_2t+\alpha-\overline{2m+1}\delta)$$
$$=\tfrac{1}{2}\mathrm{A}^2c^2f^2b^{2(n+m)}e^{-2p_1t}e^{2(m+n+1)\kappa d}$$
$$\times\left\{\cos[2(m-n)\delta]-\cos 2[p_2t+\alpha-(m+n+1)\delta]\right\}. \quad (37)$$

Integrating,

$$\int_{\overline{2n+1}t_2}^{\infty} y_m y_n \,.\, dt = \tfrac{1}{2}\mathrm{A}^2c^2f^2b^{2(m+n)}e^{2(m+n+1)\kappa d}$$
$$\times\left[-\frac{e^{-2p_1t}\cos 2(m-n)\delta}{2p_1}+\frac{e^{-2p_1t}}{2\eta}\cos\{2(p_2t+\alpha)+\chi-2(m+n+1)\delta\}\right]_{\overline{2n+1}t_2}^{\infty}.$$

The expression in the square brackets vanishes at the upper limit; so we have, substituting $\eta\cos\chi$ for p_1 in the denominator of the first fraction,

$$\int_{\overline{2n+1}t_2}^{\infty} y_m y_n \,.\, dt = \frac{1}{4\eta}\mathrm{A}^2c^2f^2b^{2(m+n)}e^{2(m+n+1)\kappa d}$$
$$\times e^{-2(2n+1)p_1t_2}\left\{\frac{\cos 2(m-n)\delta}{\cos\chi}-\cos[2(n-m)p_2t_2+2\alpha+\chi-2(m+n+1)\psi]\right\}. \quad (38)$$

If we put $m=n$, we get

$$\int_{\overline{2n+1}t_2}^{\infty} y_n^2\, dt = \frac{1}{4\eta}\mathrm{A}^2c^2f^2b^{4n}e^{(4n+2)\kappa d}e^{-(4n+2)p_1t_2}$$
$$\times\left\{\sec\chi-\cos[2\alpha+\chi-(4n+2)\psi]\right\}. \quad (39)$$

Having now got the integrals, we must next perform the summations indicated in (35). Let us take the y_n^2 integrals first: we have to sum the expression on the right-hand side of (39) from $n=0$ to $n=\infty$. The two terms in the bracket are best taken separately: the first forms a simple geometric series whose sum is

$$\frac{1}{4\eta}\mathrm{A}^2\,.\,c^2f^2\,.\,\frac{e^{2(\kappa d-p_1t_2)}\sec\chi}{1-b^4e^{4(\kappa d-p_1t_2)}}. \quad . \quad . \quad . \quad . \quad . \quad (40)$$

The second term requires different treatment, as the cosine is a function of n. We may take the cosine to be the real part of

$$e^{i(2\alpha+\chi-\overline{4n+2}\psi)},$$

and thus obtain again a geometrical series, the sum of which is

$$\frac{1}{4\eta}\mathrm{A}^2 . c^2 f^2 . \frac{e^{2(\kappa d-p_1 t_2)} . e^{i(2\alpha+\chi-2\psi)}}{1-b^4 e^{4(\kappa d-p_1 t_2)} e^{-4i\psi}} .$$

This is rationalized by multiplying numerator and denominator by $1-b^4 e^{4(\kappa d-p_1 t_2)} e^{4i\psi}$; and to further abbreviate the expression we will write

$$\left.\begin{aligned} b e^{\kappa d-2p_1 t_2} &= \xi, \\ b e^{\kappa d} &= \omega, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (41)$$

thus obtaining for the sum of the second terms of (39),

$$\frac{1}{4\eta}\mathrm{A}^2 c^2 f^2 . \frac{\omega\xi}{b^2} . e^{i(2\alpha+\chi-2\psi)} \frac{1-\omega^2\xi^2 e^{4i\psi}}{1-2\omega^2\xi^2\cos 4\psi+\omega^4\xi^4} .$$

Remembering that

$$\alpha = \frac{\theta}{2} - 2\psi' + \psi,$$

and writing

$$\theta - 4\psi' + \chi = \phi, \quad . \quad . \quad . \quad . \qquad (42)$$

this becomes, retaining the real terms only,

$$\frac{1}{4\eta}\mathrm{A}^2 c^2 f^2 . \frac{\omega\xi}{b^2} . \frac{\cos\phi - \omega^2\xi^2\cos(\phi+4\psi)}{1-2\omega^2\xi^2\cos 4\psi+\omega^4\xi^4} . \quad . \qquad (43)$$

Adding (40) and (42) together, we get for I_1, the portion of the transmitted intensity due to the square terms,

$$\mathrm{I}_1 = \mathrm{A}^2 \frac{c^2 f^2 . \omega\xi}{4\eta b^2} \left\{ \frac{\sec\chi}{1-\omega^2\xi^2} - \frac{\cos\phi - \omega^2\xi^2\cos(\phi+4\psi)}{1-2\omega^2\xi^2\cos 4\psi+\omega^4\xi^4} \right\} . \qquad (44)$$

We have now to sum the product terms. We require

$$\begin{aligned} \mathrm{I}_2 &= 2 \mathop{\mathrm{S}}_{n=1}^{n=\infty} \mathop{\mathrm{S}}_{m=0}^{m=n-1} \int_{\overline{2n+1}\,t_2}^{\infty} y_m y_n \, dt \\ &= \mathrm{I}_2' - \mathrm{I}_2'', \end{aligned}$$

say; I_2' being the sum of the terms multiplied by $\sec\chi$, and I_2'' the sum of the second terms. The integrated expression is given in (38). Taking the $\sec\chi$ terms first,

$$\mathrm{I}_2' = \frac{\mathrm{A}^2 . c^2 f^2}{2\eta b^2} \mathop{\mathrm{S}}_{n=1}^{n=\infty} \omega^{2n+2} e^{-(4n+2)p_1 t_2} \sec\chi \mathop{\mathrm{S}}_{m=0}^{m=n-1} \omega^{2m} \cos 2(m-n)\delta \, ;$$

$\cos 2(m-n)\delta$ may be treated as the real part of $e^{2i(m-n)\delta}$, or

$$\omega^{2m} \cos 2(m-n)\delta = e^{-2in\delta}(\omega^2 e^{2i\delta})^m,$$

which is a geometric series whose sum from 0 to $n-1$ is

$$e^{-2in\delta}\frac{1-(\omega^2e^{2i\delta})^n}{1-\omega^2e^{2i\delta}}.$$

Multiplying numerator and denominator by $1-\omega^2e^{-2i\delta}$ to rationalize, and retaining only the real quantities in the numerator, this becomes

$$\frac{\cos 2n\delta-\omega^{2n}-\omega^2\cos(2n+2)\delta+\omega^{2n+2}\cos 2\delta}{1-2\omega^2\cos 2\delta+\omega^4}.$$

Therefore

$$\mathrm{I}_2'=\frac{\mathrm{A}^2.c^2f^2}{2\eta b^2}\,\frac{\sec\chi}{1-2\omega^2\cos 2\delta+\omega^4}\overset{n=\infty}{\underset{n=1}{\mathrm{S}}}(\cos 2n\delta-\omega^{2n}$$
$$-\omega^2\cos(2n+2)\delta+\omega^{2n+2}\cos 2\delta)\omega^{2n+2}e^{-(4n+2)p_1t_2}.$$

The first and third terms in the bracket may be summed together, as also the second and fourth. Carrying out the summation as before, we get

$$\mathrm{I}_2'=\frac{\mathrm{A}^2c^2f^2}{2\eta b^2}\,\frac{\sec\chi\,.\,\omega\xi}{1-2\omega^2\cos 2\delta+\omega^4}\left\{\frac{\xi^2(\cos 2\delta-\xi^2)-\omega^2\xi^2(\cos 4\delta-\xi^2\cos 2\delta)}{1-2\xi^2\cos 2\delta+\xi^4}\right.$$
$$\left.-(1-\omega^2\cos 2\delta)\frac{\omega^2\xi^2}{1-\omega^2\xi^2}\right\}.$$

Bringing the two fractions to a common denominator, $(1-2\omega^2\cos 2\delta+\omega^4)$ divides out, and

$$\mathrm{I}_2'=\frac{\mathrm{A}^2c^2f^2}{2\eta b^2}\,\frac{\sec\chi\,.\,\omega\xi}{1-\omega^2\xi^2}\,\frac{\xi^2(\cos 2\delta-\xi^2)}{1-2\xi^2\cos 2\delta+\xi^4}. \quad . \quad . \quad (45)$$

Returning now to the second half of I_2, the term not containing $\sec\chi$, we have

$$\mathrm{I}_2''=\frac{\mathrm{A}^2.c^2f^2}{2\eta b^2}\,\omega\,.\,\xi\,.\overset{n=\infty}{\underset{n=1}{\mathrm{S}}}\;\overset{m=n-1}{\underset{m=0}{\mathrm{S}}}\xi^{2n}\omega^{2m}\cos\{2(n-m)\delta-4n\psi+\phi\},$$

where we have rewritten the expressions (38) in terms of the abbreviated symbols defined by equations (36), (41), and (42). Carrying out the summation first with regard to m,

$$\mathrm{I}_2''=\frac{\mathrm{A}^2.c^2f^2}{2\eta b^2}\,\frac{\omega\xi}{1-2\omega^2\cos 2\delta+\omega^4}$$
$$\times\overset{n=\infty}{\underset{n=1}{\mathrm{S}}}\xi^{2n}[\cos(2n\delta-4n\psi+\phi)-\omega^{2n}\cos(4n\psi-\phi)$$
$$-\omega^2\cos(\overline{2n+2}\delta-4n\psi+\phi)+\omega^{2n+2}\cos(4n\psi-\phi-2\delta)\,|.$$

The first and third terms in the square bracket may be summed together, and also the second and fourth. Bringing the two fractions thus obtained to a common denominator, $(1-2\omega^2\cos 2\delta+\omega^4)$ divides out, as in the case of I_2', and we obtain as our final value of I_2''

$$I_2''=\frac{A^2.c^2f^2}{2\eta.b^2}\,\frac{\omega\xi}{1-2\omega^2\xi^2\cos 4\psi+\omega^4\xi^4}\times\frac{\left\{\begin{array}{l}\xi^2\cos(2\delta+\phi-4\psi)-\xi^4\cos\phi\\ -\omega^2\xi^4\cos(2\delta+\phi)+\omega^2\xi^6\cos(\phi+4\psi)\end{array}\right\}}{1-2\xi^2\cos(2\delta-4\psi)+\xi^4}. \quad (46)$$

Combining (44) (45) and (46) we have the total value of I_t, the intensity of the transmitted ray,

$$I_t=I_1+I_2=I_1+I_2'-I_2''$$

$$=\frac{A^2.c^2f^2}{4\eta b^2}\,\omega\xi\left\{\frac{\sec\chi(1-\xi^4)}{(1-2\xi^2\cos 2\delta+\xi^4)(1-\omega^2\xi^2)}-\frac{\left\{\begin{array}{l}(1-\xi^4)[\cos\phi-\omega^2\xi^2\cos(\phi+4\psi)]\\ -2\xi^2\sin(2\delta-4\psi)[\sin\phi-\omega^2\xi^2\sin(\phi+4\psi)]\end{array}\right\}}{(1-2\omega^2\xi^2\cos 4\psi+\omega^4\xi^4)(1-2\xi^2\cos(2\delta-4\psi)+\xi^4)}\right\}. \quad (47)$$

But we want to compare this with the intensity of the ray transmitted when there is no intervening layer of electrolyte. Calling the intensity of this ray I_0, we have for its value

$$I_0=A^2\int_0^\infty e^{-2p_1t}\sin^2 p_2t\,.\,dt=\frac{A^2}{4\eta}(\sec\chi-\cos\chi). \quad . \quad (48)$$

Dividing (47) by (48),

$$\frac{I_t}{I_0}=\frac{c^2f^2.\omega\xi}{b^2(\sec\chi-\cos\chi)}\left\{\frac{(1-\xi^4)\sec\chi}{(1-2\xi^2\cos 2\delta+\xi^4)(1-\omega^2\xi^2)}-\frac{\left\{\begin{array}{l}(1-\xi^4)[\cos\phi-\omega^2\xi^2\cos(\phi+4\psi)]\\ -2\xi^2\sin(2\delta-4\psi)[\sin\phi-\omega^2\xi^2\sin(\phi+4\psi)]\end{array}\right\}}{(1-2\omega^2\xi^2\cos 4\psi+\omega^4\xi^4)(1-2\xi^2\cos(2\delta-4\psi)+\xi^4)}\right\}. \quad (49)$$

This formula is one of considerable generality, showing the variation in the intensity of the ray transmitted through a thin absorbent plate when the incident ray is logarithmically damped. Two special cases are of interest: (1) when the plate is not conducting; (2) when the incident ray is not damped. Taking the first case,

$$\left.\begin{array}{lll}\text{if}\quad \alpha_2=0, & \psi=\psi'=0, & \delta=p_2t_2,\\ \theta=0, & \rho=1, & \omega\xi=b^2,\\ \xi=be^{-p_1t_2}, & c^2f^2=(1-b^2)^2, & \end{array}\right\} \quad . \quad . \quad . \quad (50)$$

and the expression for $\frac{I_t}{I_0}$ simplifies to

$$\frac{I_t}{I_0}=\frac{1-b^2}{1+b^2}\left[\frac{1-\xi^4+2\xi^2\sin 2\delta\cot\chi}{1-2\xi^2\cos 2\delta+\xi^4}\right]. \quad . \quad . \quad (51)$$

This case was recently worked out by Dr. Barton, and our equation (51) may be reduced to his. Dividing out by the denominator in the square bracket, we get

$$\frac{I_t}{I_0}=\frac{1-b^2}{1+b^2}\left[1-\frac{2\xi^2(\xi^2-\cos 2\delta-\cot\chi\sin 2\delta)}{1-2\xi^2\cos 2\delta+\xi^4}\right].$$

Dr. Barton's expression is*

$$\frac{I_t}{I_0}=\frac{1-b^2}{1+b^2}\left[1+2b^2e^{-\alpha t_2}\frac{(\alpha/\beta)\sin\beta t_2+\cos\beta t_2-b^2e^{-\alpha t_2}}{1-2b^2e^{-\alpha t_2}\cos\beta t_2+b^4e^{-2\alpha t_2}}\right],$$

which is equivalent to ours; his t_2 being equal to twice our t_2, and his α/β equivalent to our p_1/p_2 or $\cot\chi$.

As a second special case, suppose we are dealing with a steady simple harmonic ray instead of a damped wave-train. χ is then ninety degrees, and the other symbols take the special values

$$\left.\begin{array}{l}\chi=90^\circ \quad . \quad \sec\chi=\infty, \\ p_1=0, \quad \therefore\ \omega=\xi=be^{\kappa d}, \\ \rho=\sqrt{1+\left(\frac{\alpha^2}{p_2\beta_2}\right)^2}.\end{array}\right\} \quad . \quad . \quad . \quad . \quad (52)$$

The long second term in (49) vanishes altogether now, being divided by $(\sec\chi-\cos\chi)$, and

$$\frac{I_t}{I_0}=\frac{c^2f^2}{b^2}\frac{\xi^2}{1-2\xi^2\cos 2\delta+\xi^4}. \quad . \quad . \quad . \quad (53)$$

If in this case we again put $\alpha_2=0$, we have

$$\omega=\xi=b,$$

$$\delta=p_2t_2;$$

and so if the plate be a non-conductor,

$$\frac{I_t}{I_0}=\frac{c^2f^2}{1-2b^2\cos 2p_2t_2+b^4}, \quad . \quad . \quad . \quad . \quad (54)$$

---

* Proc. Roy. Soc. vol. liv. p. 92; 'Thesis,' p. 13.

which is the ordinary expression for the ray transmitted through a thin plate.

The general expression (49) is too complex to allow of an offhand statement of its form. One case was, however, worked out in full arithmetically. The values of the chief constants chosen were

$$\frac{\beta_2}{\beta_1}=70,$$

sp. resistance of electrolyte = 5100 ohm-centim.,

log. decrement of wave-train = 0·4,

wave-length = λ_1 = 9 metres.

These gave the following values for some of our symbols :—

$$\chi=86^\circ\ 21'\ 26'',$$

$$\theta=\ 8^\circ\ 44'\ 57'',$$

$$\kappa d=-\frac{d}{\lambda_1}(\cdot673402),$$

$$p_1t_2=3\cdot3676\ \frac{d}{\lambda_1},$$

$$p_2t_2=3017^{\circ}\cdot825\ \frac{d}{\lambda_1},$$

$$b=\cdot78705,\quad cf=\cdot38167,$$

$$\log\xi=\bar{1}\cdot8960008-\frac{d}{\lambda_1}(3\cdot21751421),$$

$$\log\omega\xi=\bar{1}\cdot9920016-\frac{d}{\lambda_1}(3\cdot5099681),$$

$$\psi=1^\circ\ 3'\ 26'',\quad \psi'=28'\ 17'',$$

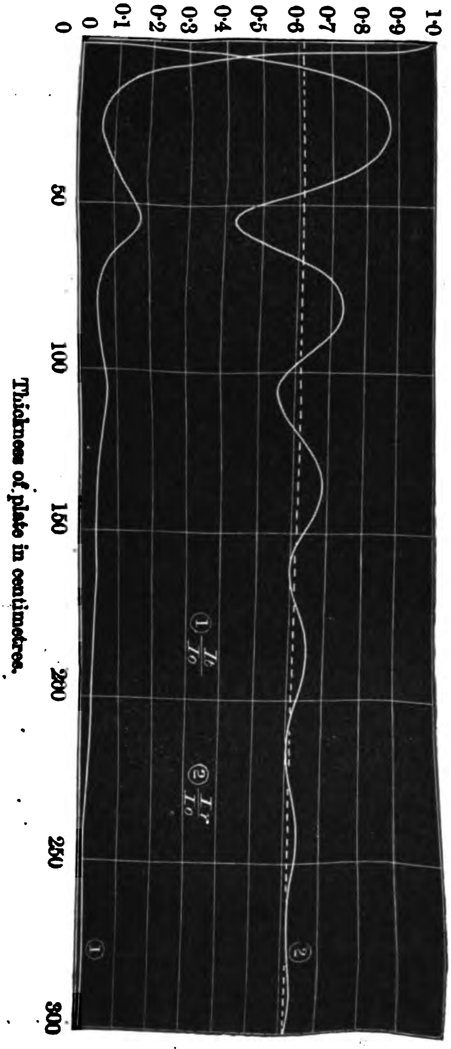
$$\rho=1\cdot0018.$$

The phase-changes at both surfaces are in this case so small that one would not expect any great shifting of the maxima in the transmission-curve, (1) (fig. 3): the maxima appear to occur rather early, but one can hardly say more. I find (49) too complex to get anything out of it by differentiation.

Fig. 3.

Curves showing the variation of $\frac{I_t}{I_0}$ and $\frac{I_r}{I_0}$ with the thickness of the plate.

Ratio of dielectric constants $= \frac{\beta_2}{\beta} = 70$. Sp. resistance of plate 5100 ohm-centim.



V. *The Intensity of the Reflected Ray.*

We will now proceed to calculate the intensity of the reflected ray. As before, let the incident wave be

$$A\, e^{p(t-\sqrt{\beta_1}x)}.$$

A portion of this incident wave is at once reflected, namely

$$Y=A\,.\,b\,.\,e^{p(t+\sqrt{\beta_1}x)}\,e^{-i\psi}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (55)$$

A second portion enters the electrolyte and reaches the second surface in the form

$$A\,.\,c\,.\,e^{p(t-qd)}\,e^{i(\theta/2-\psi')},$$

is there reflected, reaches the first surface again and emerges at time $2t_2$,

$$y_1=-A\,.\,bcf\,.\,e^{-2pqd}\,e^{p(t+\sqrt{\beta_1}x)}\,e^{i(\theta/2-2\psi'-\psi)}.$$

The next wave emerges after three internal reflexions at time $4t_2$,

$$y_2=-A\,.\,b^3cf\,.\,e^{-4pqd}\,e^{p(t+\sqrt{\beta_1}x)}\,e^{i(\theta/2-2\psi'-3\psi)},$$

and so on; the expression for the wave emergent at time $2nt_2$ being

$$y_n=-A\,.\,b^{2n-1}\,cf\,.\,e^{-2npqd}\,e^{p(t+\sqrt{\beta_1}x)}\,e^{i(\theta/2-2\psi)}\,e^{i(2n-1)\psi}. \quad . \quad (56)$$

Now

$$pq=\eta\sqrt{\beta_2\rho}\left[i\sin\left(\frac{\theta}{2}+\chi\right)-\cos\left(\frac{\theta}{2}+\chi\right)\right].$$

Inserting this value in (56), and using our previous abbreviations,

$$\kappa=\eta\sqrt{\beta_2\rho}\cos\left(\frac{\theta}{2}+\chi\right), \quad \alpha=\left(\frac{\theta}{2}-2\psi'+\psi\right), \quad . \quad (33)$$

$$\delta=p_2t_2+\psi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

and retaining only the sine terms, we have

$$y_n=-A\,cf\,b^{2n-1}\,e^{2n\kappa d}\,e^{-p_1t}\sin(p_2t+\alpha-2n\,\delta). \quad . \quad (57)$$

It is to be noted that the first reflected wave, Y, does not fall into this series so the general expression for the reflected intensity will be

$$\begin{aligned} I_r = \mathop{\mathrm{S}}_{n=1}^{n=\infty}\int_{2nt_2}^{\infty} y_n^2\,dt + 2\mathop{\mathrm{S}}_{m=1}^{m=n-1}\mathop{\mathrm{S}}_{n=2}^{n=\infty}\int_{2nt_2}^{\infty} y_m y_n\,dt \\ + \int_0^{\infty} Y^2\,dt + 2\mathop{\mathrm{S}}_{n=1}^{n=\infty}\int_{2nt_2}^{\infty} Y y_n\,dt. \quad . \quad . \quad (58) \end{aligned}$$

Multiplying out $y_m y_n$ we get

$$\begin{aligned} y_m y_n = \tfrac{1}{2}A^2 c^2 f^2 b^{2(m+n-1)}\,e^{2(m+n)\kappa d}\,e^{-2p_1t} \\ \cos 2(m-n)\delta - \cos[2(p_2t+\alpha)-2(m+n)\delta]\}\,; \quad (59) \end{aligned}$$

and integrating from $t=2nt_2$ to $t=\infty$,

$$\int_{2nt_2}^{\infty} y_m y_n\,dt=\frac{1}{4\eta}A^2c^2f^2b^{2(m+n-1)}e^{2(m+n)\kappa d}$$

$$\times e^{-4np_1t_2}\left\{\frac{\cos 2(m-n)\delta}{\cos\chi}-\cos[2(n-m)p_2t_2+2\alpha+\chi]-2(n+m)\psi\right\} \quad (60)$$

Putting $m=n$,

$$\int_{2nt_2}^{\infty} y_n^2\,dt=\frac{1}{4\eta}A^2c^2f^2b^{4n-2}e^{4n\kappa d}e^{-4np_1t_2}$$

$$\times\{\sec\chi-\cos(2\alpha+\chi-4n\psi)\}. \quad . \quad . \quad (61)$$

The summation of (61) from $n=1$ to $n=\infty$ is performed in exactly the same way as that of the analogous expression for I_t in equations (39) to (44). The result is

$$\mathop{S}_{n=0}^{n=\infty}\int_{2nt_2}^{\infty} y_n^2dt=\frac{A^2c^2f^2}{4\eta b^2}\omega^2\xi^2$$

$$\times\left\{\frac{\sec\chi}{1-\omega^2\xi^2}-\frac{\cos(\phi-2\psi)-\omega^2\xi^2\cos(\phi+2\psi)}{1-2\omega^2\xi^2\cos 4\psi+\omega^4\xi^4}\right\} \quad . \quad (62)$$

The summation of the product integrals in (60) is also analogous to that of the product integrals in I_t given in equations (44) to (46). Taking the integral in two parts as before, we have for the sum of the terms containing $\sec\chi$:—

$$\frac{A^2c^2f^2}{2\eta b^2}\omega^2\xi^2\sec\chi\frac{\xi^2(\cos 2\delta-\xi^2)}{(1-\omega^2\xi^2)(1-2\xi^2\cos 2\delta+\xi^4)}; \quad . \quad (63)$$

and for the sum of the second terms, those not containing $\sec\chi$:—

$$\left.\begin{aligned}&\frac{A^2c^2f^2}{2\eta b^2}\frac{\omega^2\xi^2}{1-2\omega^2\xi^2\cos 4\psi+\omega^4\xi^4}\\ &\times\frac{\xi^2\cos(2\delta-6\psi+\phi)-\xi^4\cos(\phi-2\psi)-\omega^2\xi^4\cos(2\delta-2\psi+\phi)+\omega^2\xi^6\cos(2\psi+\phi)}{1-2\xi^2\cos 2\delta+\xi^4}\end{aligned}\right\} (64)$$

Adding together (62) (63) and (64), bringing the second half of (62) and (64) to a common denominator and simplifying, we get the expression for that portion of I_r which is a function of the uniform series of y's only. Calling it I'_r, and dividing out by I_0 the "intensity" of the incident ray, we get :—

$$\frac{\mathrm{I}'_r}{\mathrm{I}_0}=\frac{c^2f^2\,.\,\omega^2\xi^2}{b^2(\sec\chi-\cos\chi)}\left\{\frac{(1-\xi^4)\sec\chi}{(1-2\xi^2\cos 2\delta+\xi^4)(1-\omega^2\xi^2)}\right.$$

$$-\frac{(1-\xi^4)\{\cos(\phi-2\psi)-\omega^2\xi^2\cos(\phi+2\psi)\}}{(1-2\omega^2\xi^2\cos 4\psi+\omega^4\xi^4)}$$

$$\left.\frac{-2\xi^2\sin(2\delta-4\psi)\{\sin(\phi-2\psi)-\omega^2\xi^2\sin(\phi+2\psi)\}}{(1-2\xi^2\cos(2\delta-4\psi)+\xi^4)}\right\},\quad(65)$$

an expression very similar to that for $\mathrm{I}_t/\mathrm{I}_0$ given in equation (49). Reverting now to the terms containing Y in (58), let us evaluate

$$2\overset{n=\infty}{\underset{n=1}{\mathrm{S}}}\int_{2nt_2}^{\infty}\mathrm{Y}\,.\,y_n\,dt.$$

Rationalizing (55) we have

$$\mathrm{Y}=\mathrm{A}b\,.\,e^{-p_1t}\sin(p_2t-\psi).\quad . \quad . \quad . \quad (66)$$

The expression for y_n is given in (56): multiplying up

$$\mathrm{Y}y_n=-\tfrac{1}{2}\mathrm{A}^2cf\omega^{2n}e^{-2p_1t}[\cos(2n\delta-\alpha-\psi)-\cos(2p_2t+\alpha-\psi-2n\delta)].$$

Integrating from $2nt_2$ to infinity, and writing for brevity

$$\Delta=\alpha-\psi+\chi,\quad . \quad . \quad . \quad . \quad . \quad . \quad (67)$$

we get

$$\int_{2nt_2}^{\infty}\mathrm{Y}y_n\,dt=-\mathrm{A}^2\,.\,\frac{cf}{4\eta}\,.\,\xi^{2n}$$

$$\times[\sec\chi\,.\,\cos(2n\delta-\alpha-\psi)-\cos\{2n(p_2t_2-\psi)+\Delta\}].$$

Summing this from $n=1$ to $n=\infty$, and multiplying by two,

$$2\overset{n=\infty}{\underset{n=1}{\mathrm{S}}}\int_{2nt_2}^{\infty}\mathrm{Y}\,.\,y_n\,dt=-\mathrm{A}^2\frac{cf}{2\eta}\,.\,\xi^2$$

$$\times\left[\frac{\sec\chi\{\cos(2\delta-\alpha-\psi)-\xi^2\cos(\psi+\alpha)\}}{1-2\xi^2\cos 2\delta+\xi^4}\right.$$

$$\left.-\frac{\cos(\Delta+2\delta-4\psi)-\xi^2\cos\Delta}{1-2\xi^2\cos(2\delta-4\psi)+\xi^4}\right].\quad . \quad (68)$$

Calling this I''_r, and dividing through by I_0 we get

$$\frac{\mathrm{I}''_r}{\mathrm{I}_0}=\frac{-2cf\,.\,\xi^2}{\sec\chi-\cos\chi}\left\{\frac{\sec\chi\{\cos(\psi+\alpha-2\delta)-\xi^2\cos(\psi+\alpha)\}}{1-2\xi^2\cos 2\delta+\xi^4}\right.$$

$$\left.-\frac{\cos(\Delta+2\delta-4\psi)-\xi^2\cos\Delta}{1-2\xi^2\cos(2\delta-4\psi)+\xi^4}\right\}.\quad . \quad (69)$$

The remaining portion of I_r is

$$I_r''' = \int_0^\infty Y^2\,dt = \int_0^\infty A^2 b^2 e^{-2p_1 t} \sin^2(p_2 t - \psi)\,dt$$

$$= \frac{A^2 b^2}{4\eta}\{\sec\chi - \cos(\chi - 2\psi)\}.$$

Dividing out by I_0,

$$\frac{I_r'''}{I_0} = \frac{b^2[\sec\chi - \cos(\chi - 2\psi)]}{\sec\chi - \cos\chi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (70)$$

This last expression is independent of the thickness of the slab of electrolyte.

The total expression for $\frac{I_r}{I_0}$ is (65) + (69) + (70), or rewriting these equations,

$$\frac{I_r}{I_0} = \frac{c^2 f^2 . \omega^2 \xi^2}{b^2(\sec\chi - \cos\chi)} \left\{ \frac{(1-\xi^4)\sec\chi}{(1-2\xi^2\cos 2\delta + \xi^4)(1-\omega^2\xi^2)} \right.$$
$$\left. - \frac{\left\{ \begin{array}{l} (1-\xi^4)[\cos(\phi - 2\psi) - \omega^2\xi^2\cos(\phi + 2\psi)] \\ -2\xi^2 \sin(2\delta - 4\psi)[\sin(\phi - 2\psi) - \omega^2\xi^2\sin(\phi + 2\psi)] \end{array} \right\}}{(1 - 2\omega^2\xi^2\cos 4\psi + \omega^4\xi^4)(1 - 2\xi^2\cos(2\delta - 4\psi) + \xi^4)} \right\}$$
$$-2\frac{cf . \xi^2}{\sec\chi - \cos\chi}\left\{ \frac{\sec\chi[\cos(\psi + \alpha - 2\delta) - \xi^2\cos(\psi + \alpha)]}{1 - 2\xi^2\cos 2\delta + \xi^4} \right.$$
$$\left. - \frac{\cos(\Delta + 2\delta - 4\psi) - \xi^2\cos\Delta}{1 - 2\xi^2\cos(2\delta - 4\psi) + \xi^4} \right\}$$
$$+ \frac{b^2[\sec\chi - \cos(\chi - 2\psi)]}{\sec\chi - \cos\chi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (71)$$

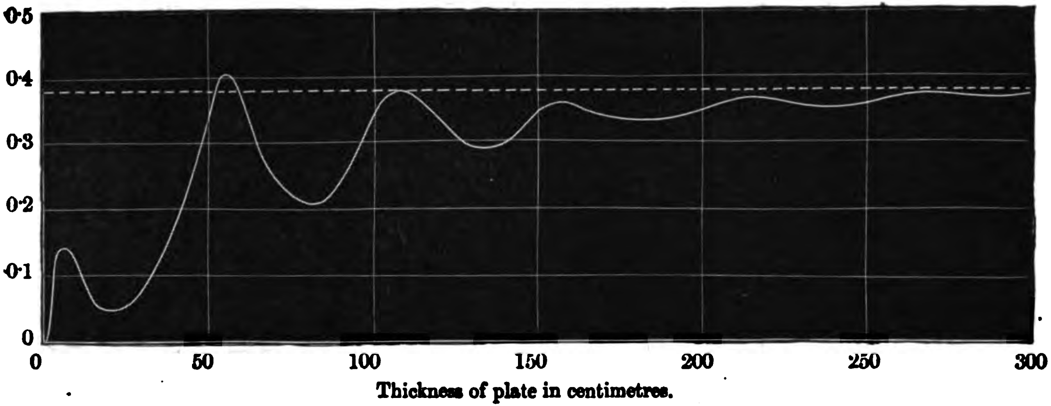
As a matter of arithmetic this expression is fairly quickly calculable if $\frac{I_t}{I_0}$ has been already worked out; a large number of the constants, &c., are the same in the two cases. The curve (2) (fig. 3) has been calculated from the same data as were given on p. 326; the two curves $\frac{I_t}{I_0}$ and $\frac{I_r}{I_0}$ may be thus compared. In the former the maxima were slightly shifted back, in the latter the minima are slightly shifted forward. The proportion of energy absorbed by the plate is

$$1 - \left(\frac{I_t + I_r}{I_0}\right).$$

The curve thus deduced from $\frac{I_t}{I_0}$ and $\frac{I_r}{I_0}$ is shown in fig 4.

Fig. 4.

Curve showing the variation in the energy absorbed by the plate $=1-\frac{I_t+I_r}{I_0}$.



As $\dfrac{I_t}{I_0}$ asymptotes to zero, and $\dfrac{I_r}{I_0}$ asymptotes to $\dfrac{I_r'''}{I_0}$ (70), $\left\{1-\dfrac{I_t+I_r}{I_0}\right\}$ asymptotes towards the value $1-I_r'''/I_0$; that is to say, when the layer of electrolyte gets very thick all is absorbed but the ray reflected from the first surface.

The expression for $\dfrac{I_r}{I_0}$ given in (71) may be checked by putting a_2 zero. Taking the three parts (65) (69) (70) separately, the first becomes at once

$$b^2\frac{I_t}{I_0},$$

where $\dfrac{I_t}{I_0}$ is the expression given in (51) or the following equation. The second part reduces to

$$(1-b^2)\,\frac{2\xi^4-2\xi^2\cos 2\delta-2\xi^2\sin 2\delta\,.\cot\chi}{1-2\xi^2\cos 2\delta+\xi^4}=1-b^2-(1+b^2)\,\frac{I_t}{I_0}.$$

The third part gives simply b^2. Adding up we get

$$\left(\frac{I_r}{I_0}\right)_{a_2=0}=b^2\frac{I_t}{I_0}+1-b^2-(1+b^2)\frac{I_t}{I_0}+b^2$$

$$=1-\left(\frac{I_t}{I_0}\right)_{a_2=0}.$$

The expression for $\dfrac{I_r}{I_0}$ also becomes greatly simplified if we take the incident ray to be non-damped. In this case

$$\sec\chi=\infty,\quad \omega=\xi=be^{\kappa d}$$

as before, and

$$\frac{I_r}{I_0}=\frac{c^2f^2}{b^2}\,\frac{\xi^4}{1-2\xi^2\cos 2\delta+\xi^4}$$

$$-2cf\,.\,\xi^2\,.\,\frac{\cos(\psi+a-2\delta)-\xi^2\cos(\psi+a)}{1-2\xi^2\cos 2\delta+\xi^4}$$

$$+b^2.\qquad\qquad (71a)$$

If we now put $a_2=0$, we have $\omega=\xi=b$, and $\delta=p_2t_2$, and so on, as given on p. 325, and the expression becomes

$$\frac{I_r}{I_0}=\frac{c^2f^2b^2}{1-2b^2\cos 2p_2t_2+b^4}$$

$$-\ 2cfb^2\,\frac{\cos 2p_2t_2-b^2}{1-2b^2\cos 2p_2t_2+b^4}$$

$$+\ b^2$$

$$=\frac{2b^2(1-\cos 2p_2t_2)}{1-2b^2\cos 2p_2t_2+b^4}, \quad . \quad . \quad . \quad . \quad (71\,b)$$

which is the ordinary expression for 'Newton's Rings by Reflexion.'

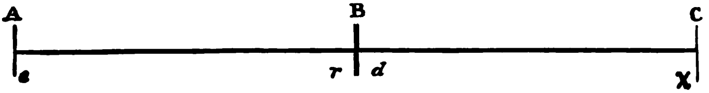
VI. *Discussion of an Experimental Case and a Correction.*

This section is independent of the rest of the paper, being devoted to the discussion of a correction necessary in the experimental case mentioned at the beginning.

It has been stated already in the introduction that the theory, sections IV. & V., does not give numerical results agreeing closely with the experimental ones. For all the values of β_2/β_1 I tried the calculated points lay continually below the experimental determinations. Dr. Barton found exactly the same peculiarity in his analogous experiments, and suggested that it might be due to the coursing of the wave-trains backwards and forwards along the wire circuit between the oscillator and the closed end. Working from this idea he arrived at a correction formula*, which, however, is not immediately applicable to our case. The following analysis is equivalent to Dr. Barton's though differing in method.

Let ABC (fig. 5) represent our circuit, B being the electrolyte, A the oscillator, C the closed end.

Fig. 5.



Let r and d be the reflexion and transmission coefficients at the electrolyte, with regard to energy, so that

$$I_t=tI_0,\quad I_r=rI_0.$$

Let e and χ be similar coefficients for the two halves of the wire circuit—reduction coefficients covering loss of energy due either to damping by the imperfectly conducting wires or to imperfect reflexion at the ends of the circuit.

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* 'Thesis,' p 16, section V.

If then

T_n is the intensity of the n^{th} train emerging from B towards C,

R_n is the intensity of the n^{th} train reflected from B towards A,

we have

$$\left.\begin{aligned} T_{n+1} &= ed\,R_n + r\chi\,T_n \\ R_{n+1} &= d\chi\,T_n + re\,R_n \end{aligned}\right\} \quad \ldots\ldots \quad (1)$$

The effect on the electrometer is proportional to

$$\overset{n=\infty}{\underset{n=0}{S}}(1+\chi)T_n,$$

so we have to sum a finite-difference series.

Let

$$\left.\begin{aligned} T_n &= Ab^n \\ R_n &= Bb^n \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (2)$$

Rewriting (1) with these values of T_n and R_n, we have

$$\left.\begin{aligned} Ab &= ed\ B + r\chi\,A, \\ Bb &= d\chi\,A + re\ B, \end{aligned}\right\}$$

whence, eliminating A and B,

$$b^2 - br(e+\chi) + e\chi(r^2-d^2) = 0. \quad \ldots \quad (3)$$

This is an equation to determine b. Suppose b_1 and b_2 to be the roots; A_1 A_2, B_1 B_2 being the corresponding values of A and B. We have then

$$b_1+b_2=r(e+\chi), \quad b_1b_2=(r^2-d^2)\,e\chi. \quad \ldots \quad (4)$$

$$\left.\begin{aligned} T_n &= A_1b_1^n + A_2b_2^n \\ R_n &= \frac{d\chi}{b_1-re}A_1b_1^n + \frac{d\chi}{b_2-re}A_2b_2^n \end{aligned}\right\} \quad \ldots\ldots \quad (5)$$

From this last equation,

$$\left.\begin{aligned} T_0 &= dI_0 = A_1 + A_2, \\ R_0 &= rI_0 = d\chi\left(\frac{A_1}{b_1-re} + \frac{A_2}{b_2-re}\right), \end{aligned}\right\} \quad \ldots\ldots \quad (6)$$

The total effect on the electrometer is consequently proportional to E where

$$E=(1+\chi)\mathop{S}_{0}^{\infty} T_n=(1+\chi)\left\{\frac{A_1}{1-b_1}+\frac{A_2}{1-b_2}\right\}$$

$$=(1+\chi)\left\{\frac{A_1+A_2-(b_2A_1+b_1A_2)}{1-(b_1+b_2)+b_1b_2}\right\}.$$

And from (6),

$$rI_0=d\chi\left\{\frac{b_2A_1+b_1A_2-re(A_1+A_2)}{b_1b_2-re(b_1+b_2)+r^2e^2}\right\}.$$

But by the relations (4),

$$1-(b_1+b_2)+b_1b_2=1-r(e+\chi)+e\chi\,(r^2-d^2),$$

$$b_1b_2-re(b_1+b_2)+r^2e^2=-e\chi d^2,$$

whence

$$-edrI_0=b_2A_1+b_1A_2-red\,I_0,$$

or

$$b_2A_1+b_1A_2=0. \quad \ldots\ldots \quad (7)$$

Thus, finally,

$$E=(1+\chi)\frac{dI_0}{1-r(e+\chi)+e\chi(r^2-d^2)},$$

$$E_0=(1+\chi)\frac{I_0}{1-e\chi},$$

and

$$\frac{E}{E_0}=\frac{(1-e\chi)d}{1-r(e+\chi)+e\chi(r^2-d^2)}. \quad \ldots\ldots \quad (8)$$

$\frac{E}{E_0}$ is an ordinate of the experimental curve. d and r are ordinates of our calculated transmission and reflexion curves. If then we determine $\frac{E}{E_0}$, d, and r for the different thicknesses of the electrolyte, we shall have by substituting their values in (8) a pair of simultaneous equations for the determination of e and χ.

This process only led to impossibilities for all values of β_1/β_2 and the log. dec. of the wave-train that were tried. Either $e\chi$ became greater than unity or negative, or $e+\chi$ became negative.

It may be noted that this correction did not work very successfully in Dr. Barton's case either. His method of applying it was, however, different: having formed an experimental estimate of the rate of decrease of the total energy of a wave-train by its passage along the imperfectly conducting wires, he assumed that there was perfect reflexion at both ends of the circuit, and thence calculated the correction to be applied to the experimental curve. The corrected curve obtained in this way lay below the calculated curve. Taking two points at random on his curves, I tried to calculate $e\chi$ and $e+\chi$ by my method. The results were again impossible.

It must be remembered that in both these cases more than one of the constants of the theoretical curve were simple guesses, γ and β_2/β_1 in my case were both only approximately known. In trying to make things square by the correction of (8), we may have been attempting the impossible and rightly got irrational results. I need not dwell at greater length on this point: possible causes of error are numerous. The non-agreement of experimental results with the equations does not of course prove the wrongness of the latter, but only the wrongness of their application to the case.

I am compelled to admit that, considering the positions of the maxima in my experimental curves are dependent on the phase-changes and on the correction we have been discussing —possibly also on other uneliminated disturbances—no great weight can be attached to the accuracy of the values of the dielectric constants for water, alcohol, &c., deduced on the assumption that such corrections were negligible *.

VII. *The Numerical Value of some of the previous Results.*

When the expressions in sections II. and III. had been obtained, the question at once arose, how far the values of b, c, f, ψ, ψ', and so on might be practically affected by possible variations in the rate of damping of the incident ray. In working with ordinary oscillators are changes likely to become important or to remain quite negligible? In working with light are differences likely to be appreciable between flashes and steady rays?

As regards oscillator wave-trains, the damping should certainly be taken into account. The second question, however, must, I think, be answered in the negative, for the simple reason that one cannot get a quick enough flash †. Even an electric spark lasts for thousands or millions of the vibrations of violet light: the rays from it would be practically steady, not damped.

The set of curves in fig. 6 is drawn for a steady ray, wave-length one metre. It illustrates the variation in b (the ratio of the transmitted to the incident amplitude at the surface of an infinitely thick slab), when the conductivity and dielectric constant of the slab vary. Curve (1) is drawn for a non-conducting slab, curve (2) for a slab of conductivity $\cdot 001 \times 10^{-9}$ C.G.S. units, and curve (3) for a slab of conductivity $\cdot 01 \times 10^{-9}$ or ten times the last. These conductivities are all extremely low, that of a 5 p.c. copper sulphate or zinc sulphate solution being roughly $\cdot 2 \times 10^{-9}$. The curves show very well how rapidly the conductivity of the reflecting plate grows in importance relatively to the dielectric constant even for great wave-lengths.

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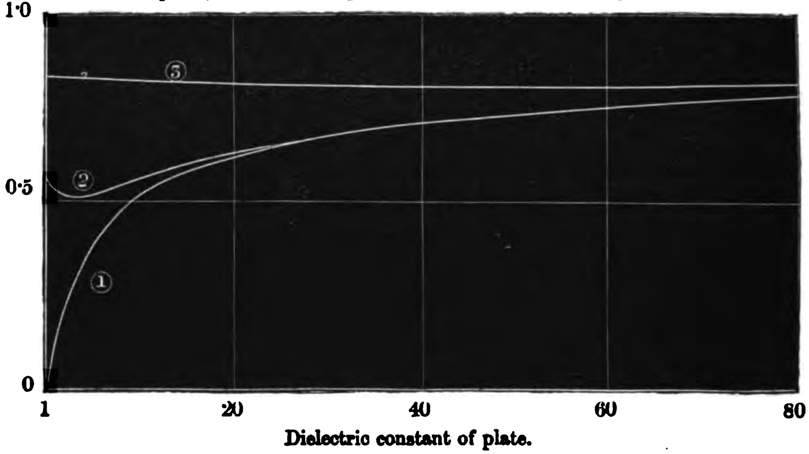
* Phil. Mag. vol. xxxvi. p. 539; Wied. *Ann.* vol. l. p. 748.

† Unless light be itself an aggregate of damped wave-trains.

Fig. 6.

Curves showing the variation in "b" with the dielectric constant and conductivity of the plate, for an undamped wave-train. Wave-length 100 cms.



(1) For a substance of zero conductivity
(2) " " conductivity $\cdot 001 \times 10^{-9}$
(3) " " " $\cdot 010 \times 10^{-9}$

$\left.\right\} \beta_1 = 1.$

But if we take the case of a charge vibrating on an isolated perfectly conducting sphere, the amplitude falls to $e^{-\frac{2\pi}{\sqrt{3}}}$ or about $\frac{1}{38}$ of its original value in the time occupied by a complete vibration*: this gives us $\chi = 54° \, 44' \, 8''$. Let us use this as an example of a damped wave-train to compare with the steady ray, retaining the same wave-length—1 metre—corresponding to a sphere about a foot in diameter.

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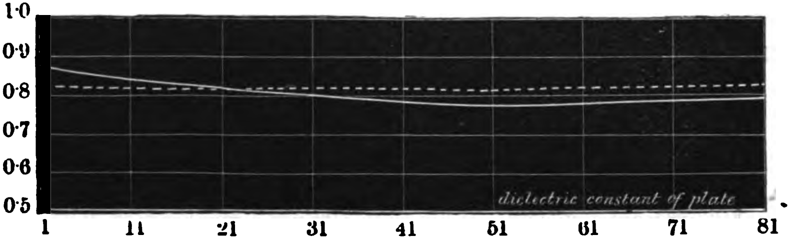
* J. J. Thomson, 'Recent Researches,' p. 370.

The curve (1) for *b* corresponding to a non-conducting plate would be the same in both cases. The curves (3) corresponding to a plate of conductivity $\cdot 01 \times 10^{-9}$ are shown together in fig. 7. *b* is at first greatest for the damped wave-train, but as the dielectric constant is increased this ratio is reversed. Physically speaking, this has very little meaning: any actual method would measure the energy of the reflected ray, and it has been shown * that the energy is a function of the phase-change, the phase-change being itself a function of the rate of damping of the wave-train. Taking the phase-changes, ψ, first, I calculated them for the steady ray, for the damped ray with which we are dealing, and the conductivity $\cdot 01 \times 10^{-9}$. The results are given together in fig. 8. For the lower values of the dielectric constant, ψ for

Fig. 7.

Comparison of the values of "*b*" for damped and undamped wave-trains.

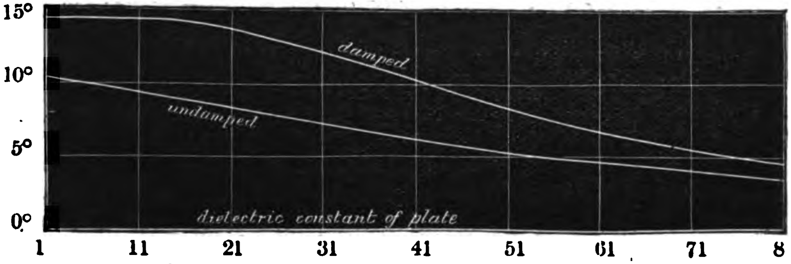


--- undamped. ——— damped. $\chi = 54° 44' 8''$.

Conductivity of plate $= \cdot 01 \times 10^{-9}$. Wave-length in either case = 100 cms. $\beta_1 = 1$.

Fig. 8.

ψ for damped and undamped wave-trains.



Conductivity $\cdot 01 \times 10^{-9}$. $\beta_1 = 1$. $\lambda_1 = 100$ cms. $\chi = 54° 44' 8''$.

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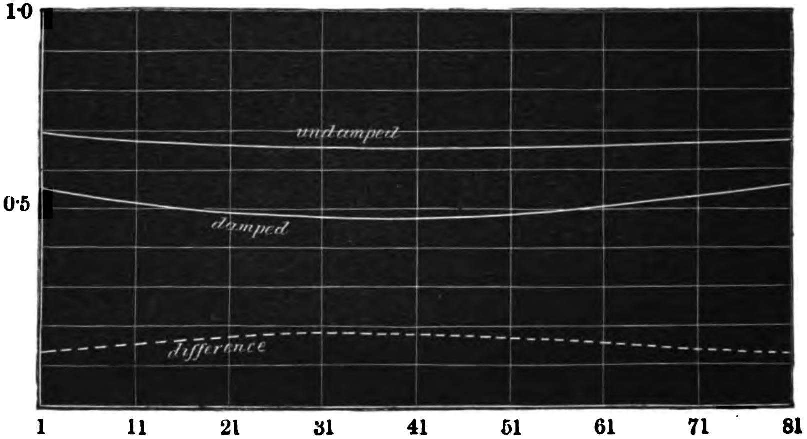
* Equation (70).

the damped wave-train is about half as large again as for the steady ray.

Utilizing these values of ψ for calculating the intensity of the reflected ray, we get the pair of curves in fig. 9. The result is striking. The energy of the reflected waves for the steady ray is from 15–20 p. c. of the incident energy greater than for the damped ray.

Fig. 9.

Curves showing the difference between the intensities of the portions of damped and undamped wave-trains reflected from an infinitely thick plate of conductivity $\cdot 01 \times 10^{-9}$.



Wave-length = 100 cms. $\chi = 54^\circ\ 44'\ 8''$. $\beta_1 = 1$.

Experimental evidence for these results would be very interesting; but, so far as I am aware, there is none whatever. In cases where χ was taken between 80° and 90°, the alterations would be much smaller and more difficult to detect. The curves I have given only illustrate, however, a very small section of cases, even larger variations may be possible.

I am glad to have this opportunity of expressing my indebtedness to Professor Karl Pearson, to whom my best thanks are due for much advice and assistance.

TABLE *of the principal Symbols used.*

The suffix 1 refers to the dielectric; the suffix 2 to the plate. In our case, where all media are assumed to be non-magnetic,

β=dielectric constant,
$a=4\pi\times$conductivity.

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b=ratio of the reflected to the incident amplitude at the first surface of the plate.
e=the corresponding ratio at the second surface.
c=ratio of the refracted to the incident amplitude at the first surface.
f=the corresponding ratio at the second surface.
d=thickness of slab.
λ_1=wave-length in dielectric.
λ_2= " " electrolyte.
$-\psi$=the change of phase on reflexion at the first surface.
$-\psi'$= " " refraction through the second surface.
$p=-p_1+ip_2$ is defined by (4).
η, χ are defined by (9).
χ gives the rate of damping of the wave-train, being 90° for a steady ray.
ρ, θ are defined by (10).
r is " " (11).
κ, α are " " (33).
δ is " " (36).
ω, ξ are " " (41).
ϕ is " " (42).
Δ " " " (67).

$$I_t/I_0=\frac{\text{intensity of transmitted ray}}{\text{intensity of incident ray}}.$$

$$I_r/I_0=\frac{\text{intensity of reflected ray}}{\text{intensity of incident ray}}.$$

XXXIII. *On the Objective Reality of Combination Tones.* By A. W. RÜCKER, *M.A.*, *F.R.S.*, *and* E. EDSER, *A.R.C.S.*[*]

THE question of the objective existence of combination-tones has been keenly disputed. At first they were regarded as produced within the ear itself. Von Helmholtz in part adopted this view, and gave a theoretical explanation of the way in which the construction of the ear might lend itself to such a result. ('Sensations of Tone,' App. XII.) He also believed that they existed objectively when the amplitudes of the vibrations of the notes which give rise to them are so great that powers higher than the first have to be considered. He supported this view by mathematical demonstrations, and stated ('Sensations of Tone,' transl. by A. Ellis, p. 157) that he had proved their objective existence by making membranes and resonators to respond to combinational tones produced by the siren and harmonium. These views and statements have been adversely criticised by König, Bosanquet, and Preyer. A very lucid account of the controversy was given by the late Mr. Ellis in his translation of the *Tonempfindungen*, and the net result of the impression produced in his mind is shown by two notes on pages 156 and 157. He there states that the result of Mr. Bosanquet's and Prof. Preyer's experiments is to show that the combinational tones are produced in the ear itself, and that it is probable that the apparent reinforcement of the resonators noticed by Helmholtz arose from imperfect blocking of both ears when using them.

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[*] Communicated by the Physical Society: read March 22, 1895.

These statements were unqualified, and no condition was made as to the way in which the combination-tones were produced. Helmholtz, for reasons which we need not recount, regarded the siren as the best instrument for producing objective combination-tones; and we recently determined to submit the question of their existence, which seemed to be decided against him, to another experimental test.

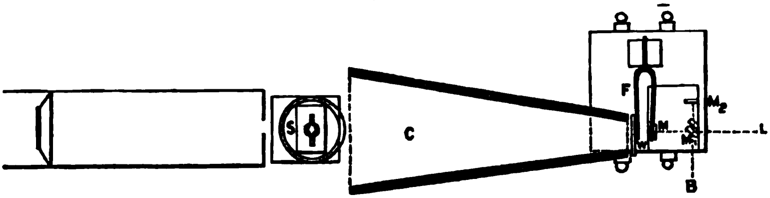
In this paper we give the result of our investigations, as far as they have at present been carried out. We do not regard them as complete, but they at all events prove that when the conditions under which we experimented are fulfilled, there can be no doubt that difference and summation-tones are produced which are capable of disturbing resonating bodies.

The resonator employed in the first instance was a tuning-fork. It is well known that this instrument is relatively difficult to excite by resonance, and it was therefore necessary to use an extremely delicate method of detecting whether it was set in motion. For this purpose a mirror attached to one of the prongs was made one of a system by which Michelson's interference-bands were produced. A movement of the prong amounting to half a wave-length of light (say 1/80,000 of an inch) would alter the length of the path of one of the interfering rays by a wave-length. A periodic vibration of this amplitude would cause the band to disappear.

It is therefore evident that an extremely minute movement could be detected. It was at first open to question whether the apparatus would not be so sensitive to accidental disturbances as to be untrustworthy. This difficulty has, however, been entirely overcome.

A plan of the apparatus is shown in fig. 1. The shank of the tuning-fork, F, is imbedded in a mass of lead. One of the prongs carries a mirror, M. To the other is attached a square of wood, W, of larger area but of the same weight as the mirror. A Lissajous' figure (an ellipse) was formed by reflexion from the mirror and from a small square of silvered glass attached to one of König's large forks adjusted to give the C of 64 complete vibrations per second, and the pitch of F was adjusted until only one beat occurred in two minutes. The pitch was thus very accurately known. A double siren, S, was placed between a large König resonator tuned to 64 vibrations and a wooden cone or pyramid, C. The end of the cone was placed about half an inch from W, which was rather larger than the narrow end of the cone. The sensitiveness of the apparatus depended in part upon the distance between W and C. If the distance was too large, the sensitiveness was diminished. If it was too small, the instrument was unduly affected by chance puffs of air even when not periodic in character.

Fig. 1.



A source of light, L, was used to form a system of interference-bands by means of the half-silvered mirror M_1, and the two mirrors M and M_2. The two interfering rays travelled over the paths $LM_1M_2M_1B$ and LM_1MM_1B respectively. The distances MM_1 and M_1M_2 were approximately equal; and since when soda-light was used a change in the length of either of the paths of $\frac{1}{2} \times 589\ \mu\mu$ would cause a dark band to shift into the position previously occupied by the next bright band, and since, further, any movement of M altered the length of the path of the ray by twice its own magnitude, it is evident that a movement of $\frac{1}{4} \times 589\ \mu\mu$, or, say, of one hundred thousandth of an inch, could be easily detected.

The fork F and the mirrors M, M_1, and M_2 rested on a square stone, which was suspended by wires and india-rubber door-fasteners from a heavily weighted beam, which itsel rested on india-rubber balls placed at a convenient height on a double pair of wooden "steps." With these precautions it was found that the bands remained tolerably steady even by day when persons were moving about the building, and when the traffic on the frost-bound road produced considerable mechanical vibrations. Even under these conditions, we have satisfied all who have seen the apparatus of the reality of the phenomena. The experiments on which we rely, however, were made on several occasions between midnight and 2 or 3 A.M. The bands were then absolutely clear and steady. They were undisturbed for many minutes at a time when the bellows were being worked and the siren was sounding loudly. It was only when a note of 64 vibrations per second was directly or indirectly produced that they vanished, and there could be no possible doubt or mistake as to whether the disturbance was or was not produced by the sound or combination of sounds under investigation.

Up to the present we have used the fork above described only. It was chosen because it was fairly stiff, and as removable metal mirrors for the production of Lissajous' figures were attached to its prongs, it was possible to replace them by the glass mirror and square of wood without altering its pitch. It would be quite possible to use properly made forks of higher pitch as resonators, and the steadiness of the bands at night is so remarkable, that we believe that if the apparatus were set up in the country, on a stone isolated from the rest of the room, the degree of sensitiveness we have attained could be far surpassed.

Tuning the Siren.

Three methods were used for determining when the siren was producing the required notes. When one of these was fairly high, the beats given by it and a standard fork were noticed, and the note could thus be kept hovering about the required pitch for a considerable time. Although with the aid of König's large forks we could apply this method to vibration-frequencies of 48 per second and upwards, it was difficult when the notes were very low to recognize the beats with sufficient certainty.

The prongs of various tuning-forks were therefore furnished with two pieces of tin-foil, which opened and closed a slit made in them twice in every complete vibration. They were also compared with a standard by the aid of a revolving cylinder, and were adjusted by weights to the required frequencies. These were so selected as to make one of the circles of holes on the siren appear stationary when viewed through the slit, if the velocity of rotation was such that the desired note or notes would be given by the same or other circles of holes. An observer watching the siren through the slit and pressing lightly on the axis with a straw, was able to adjust its speed so that the required combination of sounds was produced for several, and in some cases for many seconds at a time.

We have also projected the image of the row of holes on a screen, the cone of light passing at its narrowest part through the slit in the tinfoil screens carried by the auxiliary fork. When the upper siren was to be used, two semicircles of light mirror-glass were laid on the disk of the lower siren to which the two halves of a paper cog-wheel were fastened. The image of the cogs could thus be projected.

The third method of determining the speed of the siren depended on the use of an instrument first devised by Lord Rayleigh in 1880. A mass of air enclosed in a tube is excited by resonance, and the fact of the excitation is indicated by a light mirror set where the motion is greatest, and inclined at 45° to the direction of the air-currents. In accordance with the general law that a lamina tends to place itself perpendicular to the direction of a stream, the mirror moves when the air vibrates. In the original apparatus the amount of the movement was controlled by magnets. Since that date Professor Boys has modified the instrument by substituting a quartz-thread suspension for a silk fibre, and using the torsion of the thread instead of the directing force of the magnets. He exhibited the apparatus during a lecture delivered before the British Association in Leeds. It may be called a mirror-resonator.

Professor Boys has been good enough to make two of these instruments for us, and it was decided that one of them should respond to 161 vibrations per second. The movement of the spot of light reflected from the mirror informed us when the siren was giving this note, and this fact was utilized in one of the experiments.

Sensitiveness of the Apparatus.

The results were in general improved by laying a small strip of dry blotting-paper upon the prongs. Mere accidental disturbances died out more quickly, and the vibrations of the fork diminished more rapidly, when the notes which had produced them ceased to sound.

A forced movement could be produced in the fork by blowing directly down the collecting cone, but a small organ-pipe could be sounded, or a König's fork bowed near the opening without producing the least effect if the frequency of the note produced was not near 64 per second. In like manner many notes of two reed wind-instruments, somewhat similar in construction to the harmonium, were sounded simultaneously so that the room echoed with discordant sound, yet without producing the least effect on the steadiness of the bands.

On the other hand, when one of König's forks tuned to 64 vibrations was touched with the india-rubber covered handle of a gimlet, or was struck with a piece of gas-tubing so lightly that an observer with his ear close to the fork could not detect the fundamental note, the bands instantly disappeared.

It was therefore evident that the apparatus could respond to a vibration which was quite inaudible to a person standing by the resonating fork.

When the König fork was weighted so as to give 63·5 vibrations per second, the bands appeared and disappeared at regular intervals of two seconds, thus corresponding to the beats between the exciting and resonating forks. The bands were not disturbed when the beats exceeded 2 or 3 per second unless the exciting fork was bowed very violently. In the experiments with fainter tones, the resonating fork was only disturbed when the frequency of the exciting note agreed very exactly with its own.

As the speed of the siren was gradually increased from rest the bands always disappeared two or three times, the disturbance being no doubt caused by the upper partials as the vibration-frequency passed, in turn, the values 16, 21·3, and 32 per second. No exact measurement was made of the corresponding frequencies, as there could be no question as to whether the partials were produced or as to whether the apparatus could detect them. No such disappearance occurred when the note was higher than C, except in the case of certain spurious effects referred to below.

All the experiments were performed several times on each occasion, and on two occasions at least. The bands were sometimes produced by soda-light, and watched by an observer through a telescope.

Sometimes the electric light was used. The bands could then be projected on a screen side by side with the image of the holes or cogs. In this way information as to the note produced and as to the behaviour of the bands was simultaneously conveyed to all who watched the experiments.

Precautions.

It will not be thought remarkable that so delicate an apparatus requires careful use.

In the first place, it was necessary to be sure that the disturbance ascribed to the joint action of two notes was not produced by one or both of them when acting alone. In all cases, therefore, in which it was possible to determine the pitch of both notes separately, each note was sounded alone and carried slowly past the particular pitch at which the existence of a combination-tone was to be investigated. In general, no effect was produced; but after the apparatus had been in use for some little time, we were troubled by the fact that two notes which did not differ much from 256 and 320 vibrations respectively disturbed the bands when they were produced separately.

That these effects were spurious was evident from two facts. Firstly, the same notes had previously been sounded for a long time with the special object of determining whether they produced any effect, and had produced none. Secondly, the disturbances were evidently forced. When the fork has been disturbed by a vibration of frequency 64, it continues to oscillate for several seconds after the disturbing note has ceased. The bands alternately appear and disappear several times before the final state of rest is attained. In the case of a "spurious" effect, the bands reappear instantaneously with absolute clearness the moment the disturbing note ceases, thereby indicating a forced vibration. It was, however, a more difficult task to discover the cause than to determine the character of these disturbances. Finally, it was found that since the apparatus was first set up some cracks had opened in the wooden pyramidal collector. A tap on the side of this will disturb the bands; and when one of the cracked sides was loaded with weights the disturbance due to the 320 note was much reduced. The cracks were then cut out, the defects made good; and since that time this disturbance has entirely ceased.

The effect produced by the 256 note was due to another cause. When the pyramid was removed, the open ends of the resonance-boxes of various tuning-forks (256, 320, 384) were held near the square of wood which was attached to the fork F. It was found that the 256 fork was the only one which affected the bands, and that it only produced any result when the sounding-box was held near that part of the wood which projected beyond the end of the prong. It was therefore evident that the two ribs attached to this were not sufficient to prevent a certain flapping of the projecting part, and that this responded to a note of about 256 vibrations. The end of the collecting pyramid was then shifted a little so that the waves of sound impinged only on the more rigid part of the wooden square, and the spurious effect immediately and completely disappeared.

Of the notes which caused these troubles, the lower one was decidedly lower than the *c*′ of 256; the other corresponded very accurately with the *e*′ of 320. The fact that both these numbers are multiples of 64 may legitimately give rise to the doubt whether the fork F can be set in motion by disturbances which are multiples of its own frequency.

Even if it be admitted that such forced vibrations would be especially easy to produce, we must insist—(1) that we can distinguish (as above described) between forced and natural vibrations; (2) that when the apparatus was properly arranged such notes could be produced by the siren for long intervals of time without the least effect on the bands; (3) that two tuning-forks, of 256 and 320 vibrations respectively, have been placed within the wooden pyramid with their sounding-boxes resting on and supported by, the lower side, yet no effect was produced on the bands even when they were both sounding loudly at the same time; (4) that one of König's large forks, with a frequency of 128, was placed in front of the collecting cone and produced no effect when sounding loudly, though the slightest tap on the 64 fork caused the bands to vanish for many seconds; (5) that the 320 and 384 forks produced no effect when the pyramid was removed and they were held as above described close to the receiving prong of the fork; (6) and, lastly, that in two out of the five experiments on the difference-tones, and in all those in which the interference apparatus was used to detect summation tones, the frequencies of the notes employed were neither multiples nor sub-multiples of 64.

As in all the above experiments the resonator was in position, they also sufficed to prove that tones of 64 vibrations were not manufactured in it by the primary notes when acting singly.

If the objection is raised that, although neither note disturbed the bands when sounded alone, the effect might be due to the double disturbance produced by the two sounds, we think it sufficient to answer that we have always carried the two notes above the pitch at which the difference-tone might be expected to affect the instrument, then lowered the pitch again till the notes were too flat, and repeated this operation several times. The disturbances were only produced when the pitch was nearly, or very nearly, correct. As soon as a few beats per second were heard the bands became visible.

Having thus described the various tests which were applied to the apparatus, we may proceed to describe the experiments without dwelling further on the necessary precautions. It is sufficient to say once for all that they were adopted in each case.

The main object of the enquiry was to obtain evidence as to the objective reality of the combination-tones, and for this purpose the following experiments were arranged.

Each box of the siren had four circles of holes which could be used separately or together. The number of openings in the upper box were 9, 12, 15, and 16, and in the lower 8, 10, 12, and 18. It will be convenient to refer to these as the 9 row of holes, and so on.

Experiment I.

The 12 and 15 rows of holes in the upper box were opened, and the pitch was raised until the upper note gave slow beats with a fork of 320 vibrations per second. The lower note was then the C of 256 vibrations. The difference or beat tone of 64 vibrations affected the instrument powerfully. The experiment was tried both by night and by day. It was difficult to keep the siren exactly at the true pitch, but when the beats were very slow the bands continually disappeared, sometimes for many seconds at a time, then appeared for a moment and then disappeared again. As soon as the pitch was lost by a few beats per second, the bands remained steady and clearly visible.

The experiment was repeated with the 9 and 12 rows of holes. When the upper note was C of 256 vibrations, the lower note was 192 vibrations. The difference-tone of 64 vibrations affected the fork very powerfully.

The experiment was also modified by opening the 10 and 12 rows of holes. When the notes corresponded to 320 and 384 vibrations respectively, the bands disappeared as before.

Experiment II.

In experiment I. the frequencies of the difference-tone and of König's first lower beat-tone were identical. The experiment was therefore varied by using 8 and 18 rows of holes. The frequency of the difference-tone was thus proportional to 10, while that of König's lower beat-tone would be $18-2\times 8=2$. When the siren was revolving at the rate of

6·4 revolutions per second, the two notes corresponded to 51·2 and 115·2 vibrations per second, the difference-tone being 64.

The pitch was determined on different occasions by different methods. Firstly, by noting the beats between the higher note and a König's fork adjusted to 115·2 complete vibrations per second, and secondly, by watching the row of eight holes through a slit carried by a fork which gave 25·5 vibrations per second.

The effect was rather feebler than in the last experiment, but there was absolutely no doubt as to the objective reality of the difference-tone. The bands regularly disappeared when the required pitch was obtained, and reappeared when it was lost.

Again the 15 and 9 rows of holes were used. The difference-tone is thus proportional to 6, and König's beat-tone to $9\times 2-15=3$. When the rate of revolution was $10\cdot\dot{6}$ the two notes were 160 and 96 respectively. In this experiment the mirror-resonator which responds to 161 vibrations was employed to determine the rate of the siren. The bands and the spot of light were sometimes watched together: on another occasion one observer who could not see the bands raised his hand whenever the spot of light moved. The bands invariably disappeared at the instant that this signal was made.

Experiment III.

The next experiment was directed to determine the objective reality of König's lower beat-tone when the interval was greater than an octave. The 8 and 18 rows of holes being kept open as before, the speed was increased until the lower note was that of 256 vibrations. The upper note was then 576, and König's lower beat-tone was of $576-2\times 256=64$ vibrations.

We lay less stress on negative than on positive results; but we tried for a long time on two occasions to get evidence of the objective character of the note, but entirely failed. The pitch was determined by the beats with a 256 fork.

Experiment IV.

We next turn to observations on the summation-tone. The 8 and 10 rows of holes were opened, so that when the cover made 3·55 revolutions per second the summation-tone would be that of $18\times 3\cdot\dot{5}=64$ vibrations, The pitch of the notes given by the siren was again determined in different ways on different occasions. The summation-tone being produced in the lower box, the 15 row in the upper box was also opened, thus producing a note of $15 \times 3{\cdot}\dot{5} = 53{\cdot}\dot{3}$ vibrations per second. The required speed was determined by making the beats vanish between this note and a König's fork tuned to give 53·3 vibrations. With this method it was difficult to keep the speed constant for a length of time sufficient to disturb the resonating fork appreciably. When the pitch was altered very slowly the bands disappeared just as the right note was reached, and did not disappear at any other time during the experiment.

On another occasion the 9 and 12 rows of holes were opened, so that the summation-tone of 64 vibrations would be given when the siren made 3·05 revolutions per second. The 18 row of holes was watched through a fork of 27·2 vibrations, so that 54·4 views would be obtained while a hole moved over $18 \times 3{\cdot}05 = 54{\cdot}9$ intervals. Hence the right pitch was obtained when the holes moved slowly forwards. The bands invariably disappeared when this state of things was attained.

On a third occasion the lower cover of the siren was covered with a thin piece of silvered glass as above described, carrying a concentric circle of black paper, the edge of which was divided into 18 equidistant cogs. An image of these was produced on a screen by a lens, and made intermittent by the 27-vibrations fork. The disturbance due to the summation-tone was again and again made evident when the images of the cogs appeared to be moving slowly. In the intervals the bands were beautifully steady.

The earlier of these experiments were performed before, and the later ones after, the apparatus had been taken down and set up again in another room. They left in the minds of those who saw them no shadow of doubt as to the objective reality of a note corresponding in frequency with the summation-tone.

We now turn to experiments intended to throw light on the cause of the production of this note.

Experiment V.

It has been suggested that the summation-tone may be the difference-tone of partials. König (*Acoustique*, p. 127) remarks that it may occasion some surprise that the particular harmonics whose difference-tone corresponds to the summation-tone should be especially prominent; but he points out that in some cases the difference-tones of the lower harmonics correspond either to the fundamentals or to some of their upper partials. In the case of the fourth (3 : 4), however, König remarks that the 5th partials would give a difference-tone (5) which could be distinguished from the lower partials, and that the difference-tone of the 7th partials would give the summation-tone. Now we have already proved (Exp. IV.) that the summation-tone produced by two notes separated by the interval of a fourth (9 : 12) is objective; and if this is due to the difference-tone of the 7th partials, there seems to be no reason why the difference-tone of the 5th partials should not be objective also, and probably more intense.

We therefore increased the velocity of revolution to 4·27 per second, the 9 and 12 rows of holes being opened as before. The frequencies of the two notes were thus 38·43 and 51·24. The pitch was determined by keeping the 12 holes nearly stationary when viewed 51 times a second by aid of the 25·5 fork. The first difference-tone was 12·81, and the difference-tone of the 5th partials was 64·05. When the speed corresponding to this difference-tone was attained there were occasional flickers of the bands, so that it is possible that it has an objective existence. But, on the other hand, the effect was less than that produced by the summation-tone. The bands never disappeared for any considerable length of time, as they did when the fork responded to the summation-tone, and the experiment left no doubt in our minds that the greater effect was produced by the summation-tone.

Experiment VI.

The same point was also investigated in another way. If the summation-tone of two notes of frequencies p and q corresponds to the difference-tone of the nth partial, we must have

$$(p+q) = n(p-q),$$

where n is an integer. If, however, the 9 and 16 rows of holes were opened,

$$p+q=25, \quad p-q=7;$$

so that the summation-tone could not be produced by partials of the same order. The 10th partial of the higher note beating with the 15th of the lower note $(160-135=25)$ would indeed have the same frequency as the summation-tone, but it appears to us absurd to suppose that so improbable a combination should produce appreciable results. It is true that lower partials may give beat-tones near to the summation-tone, Thus $5 \times 16 - 6 \times 9 = 26$. But if we are to assume that any pair of partials can thus produce objective tones, the number of combinations will be so great that the fork ought to have been disturbed frequently when the note of the siren was being raised to the required pitch. As a matter of fact, when once the C of 64 vibrations was passed, so that all the partials were higher than the pitch of the resonating fork, no such disturbances were ever observed except when the difference- or summation-tone of the primaries was produced. Putting, therefore, all such fantastic combinations aside, the experiment may be regarded as a test whether the summation-tone can be produced when it cannot be due to two partials of the same order.

When the velocity of revolution was 2·56 per second, the 16 and 9 holes gave notes of 40·96 and 23·04 vibrations. The sum of these is 64. The 12 holes were viewed through a slit alternately closed and opened by a fork of 15 vibrations per second, and when the holes appeared to move slowly the summation-tone caused the bands to disappear.

In this experiment, however, the third partial of the lower note corresponds to 69·12 vibrations, and we thought it desirable to make sure that the disturbance attributed to the summation-tone was not in reality due to this partial. This was the more important, because the difference in the speeds of the siren when the summation-tone and the partial in question corresponded to 64 vibrations was very small.

Thus, when the speed was 2·56 revolutions per second each of the 12 holes would advance through 30·72 intervals in a second, and since the fork gave 30 views per second the holes would appear to move slowly forwards.

When the speed was 2·37 revolutions per second the third partial of the lower note (9 row of holes) would be $3 \times 9 \times 2{\cdot}37 = 64$, and each hole of the 12 rows would advance through 28·44 intervals—that is, would appear to recede through 1·56 intervals per second. Thus the partial would be most efficient in promoting disturbance when the holes appeared to go backward with moderate speed.

The question to be answered was whether these two disturbances could be confused with each other.

When care was taken to keep the pressure in the wind-chest the same whether one or both sets of holes were opened, the effect of the partial produced by the 9 set of holes could hardly be detected. The bands were shaken a little when the row of 12 holes appeared to move backwards, but they did not disappear; whereas they were completely wiped out by the summation-tone when the two notes were sounded.

When the pressure on the wind-chest was increased, the rate of revolution being nevertheless maintained constant by pressing lightly on the axle of the siren with a straw, the effect of the partial was more marked, but it was always produced when the holes appeared to move backwards.

On the other hand, when both notes were sounded together and when the pitch was gradually *reduced* to the desired point, the disturbance always began when the holes moved slowly forwards. If the pitch fell very slowly it was possible to note a reduction of the disturbance, followed by an increase when the holes appeared to move backwards.

We thus convinced ourselves that the effects of the two sources of disturbance could be distinguished, and that the supposed summation-tone was not due to the partial of the lower note.

Experiment VII.

We have also succeeded in demonstrating the reality of the summation-tone with a mirror-resonator constructed by Professor Boys to respond to a vibration-frequency of 576.

The rows of 15 and 12 holes being opened, notes of 320 and 256 vibrations were produced. When they were sounded separately, the mirror moved slightly. When they were sounded together, the spot of light was driven off the scale when the upper note coincided with that of a 320-vibration fork, but immediately returned when this pitch was lost.

The experiment was varied by using the 16 and 12 rows, and also the 16 and 9 rows. The summation-tone corresponds to 576 vibrations when the upper note is of 329·15 and 360 vibrations in these two cases respectively. The 320-fork was used, and the disturbance occurred in the one case when the pitch of the note was nearly the same as before, and in the other when it was about a tone higher.

We attach great importance to this corroboration of our results by an instrument of a totally different construction from that first employed.

The attempt to obtain proof of the existence of a difference-tone by means of the mirror-resonator of 161 vibrations has not been successful. The instrument is much less affected by the note to which it responds than is that which answers to 576 vibrations, even when that note is produced directly by the siren. It is, therefore, perhaps not wonderful that it gives no reliable evidence of the existence of a difference-tone.

We now sum up the results we have obtained in two tables.

Instrument. Interference Resonator.

Number of holes in siren.	Interval.	Frequencies.		Combination-tone.	König's Beat-tone.
12 and 10	Minor Third.	384	320	64 Difference-tone.	64
15 „ 12	Major Third.	320	256	64	64
16 „ 12	Fourth.	256	192	64	64
15 „ 9	Major sixth.	160	96	64	32
18 „ 8	Octave and major tone.	115·2	51·2	64	12·8
10 and 8	Major Third.	$35{\cdot}\dot{5}$	$28{\cdot}\dot{4}$	64 Summation-tone.	
12 „ 9	Fourth.	36·57	27·43	64	
16 „ 9	Minor Seventh.	40·96	23·04	64	

Instrument. Mirror Resonator.

Summation-Tones.

Number of holes in siren.	Interval.	Frequencies.		Sum.
15 and 12	Major third.	320	256	576
16 „ 12	Fourth.	329·15	246·85	576
16 „ 9	Major sixth.	360	216	576

Negative Results.

We have tried several times to obtain indications of combination-tones when the primary notes were produced by tuning-forks. Two of König's large forks adjusted to 48 and 112 vibrations produced no effect when bowed simultaneously before the collector, and, as has been stated, smaller forks giving 256 and 320 vibrations have been placed inside the collector when sounding loudly. No effect whatever was produced, and there can be no doubt that if objective combination-tones are produced in such cases they are very much less intense than those generated by the siren.

Experiments have been made with reeds and with organ-pipes, but up to the present with uncertain results in the first case and negative results in the second. We hope to investigate these cases further.

We have made several attempts to detect combination-tones of higher orders, such as $2p+q$ and $2p-q$, but without success.

Conclusion.

We may in conclusion refer to some of the suggestions which have been made to account for the combination-tones by theories other than those of Helmholtz.

König's suggestion that they are the beat-tones of upper partials has been discussed and shown to be inadequate to explain the facts of observation.

Again, it has been argued that the summation-tone is the beat-note between the second partial of the higher note (the octave) and the beat-tone of the two primaries. It follows as a matter of algebra that such an explanation must always be numerically correct, for $2a-(a-b)=a+b$, and our experiments throw no new light on the matter. It appears to us, however, that since propinquity between the sources of sound, causing a violent disturbance, is favourable to the production of combination-tones, while it is not necessary for the production of beats, the facts of experiment are in this case also in favour of von Helmholtz's views.

A still more subtle objection has been taken by Terquem (*Annales d'Ecole Normale*, 1870, p. 356). When two rows of holes are open in the siren, there may be occasions on which all the holes of both rows are opened simultaneously and others on which only one row is in action at one time. Terquem attempts to calculate the effects of irregularities such as these, but in the first place he specifically refrains from attacking the theory of Helmholtz ; secondly, he does not apply calculation to the siren of Helmholtz ; thirdly, he points out that the relatively large size of the holes in that instrument would reduce the effects he predicts ; and, lastly, he admits that his results require confirmation by experiment. Putting these points aside, however, his theory leads to the conclusion that the two notes which we have been regarding as fundamental are reinforced harmonics in a series of which the fundamental note corresponds to the greatest common measure of these frequencies. Both the summation and the difference tone must be included in such a series ; but Terquem's theory gives no reason why they should have such exceptional importance as experiment proves that they have. Lastly, as he expressly repudiates the idea that partials have an objective existence (*loc. cit.* p. 274), and includes the combination-tones in a series of partials, the experiments described by us must on this point be regarded as opposed to his views.

We think, then, that our experiments prove that von Helmholtz was correct in stating that the siren produces two objective notes the frequencies of which are respectively equal to the sum and difference of the frequencies of the fundamentals, and that our observations are also more or less opposed to the theories by which König, Appun, and Terquem have sought to account for the production of these notes.

We believe that the method we have devised is capable of greater sensitiveness. It can be extended by employing forks of different pitches, and it is quite possible that less massive forks may enable us to detect effects which have hitherto escaped us. We therefore refrain from any wide generalizations until a wider foundation of experiment has been laid.

P.S.—Since the above was written Prof. S. P. Thompson has drawn our attention to a paper by O. Lummer, published in 1886 (*Verh. phys. Gesell. Berlin*, 1886, No. 9, p. 66), which had escaped our notice, as it is not abstracted in the *Beiblätter*. Herr Lummer obtained evidence of the objective character of the summation-tone by means of the microphone.

XXXIV. *Energy Movements in the Medium separating Electrified or Gravitating Particles.* By H. N. ALLEN, *University of Nebraska, Lincoln, Neb.*

1. FARADAY and Maxwell have shown that it is possible to look on the potential energy of electric separation as residing in the surrounding dielectric, and that each of the cells, bounded by the walls of a tube of force and two neighbouring equipotential surfaces, can be looked upon as containing a certain definite amount of energy.

This energy-distribution is not in general permanent, and can only be regarded as a step towards some simpler arrangement. Thus a positive and a negative electrified body suspended in space, and acted on only by the electrical forces between them, are never in equilibrium until they are in actual contact. The energy-distribution in the dielectric changes constantly as they approach. Poynting has shown[†] how energy is transferred from one point to another in an electromagnetic field; and we are quite accustomed to think of energy as flowing from dynamo to motor through the æther, or from primary to secondary in an alternating-current transformer.

In the following pages an attempt is made to deduce a few

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[*] Communicated by the Physical Society: read March 8, 1895.

[†] Phil. Trans. 1884, Pt. II. p. 343.

of the consequences of Maxwell's suggestion with regard to energy-distribution. The changes needed in the theory in order to apply it to gravitation are also indicated.

2. If two equal charges of positive and negative electricity $+\mathrm{M}$ and $-\mathrm{M}$ are separated by a distance l, the equation to the curve in which the equipotential surface V intersects the plane of the paper is

$$\frac{\mathrm{M}}{\sqrt{y^2+(\frac{1}{2}l-x)^2}}-\frac{\mathrm{M}}{\sqrt{y^2+(\frac{1}{2}l+x)^2}}=\mathrm{V}, \quad . \quad (1)$$

the origin being the point midway between the particles, and the X-axis being the line joining this point to the positive particle.

3. The number of tubes of force proceeding from a charge M has sometimes been taken as M but more generally as $4\pi\mathrm{M}$. For graphical methods the former plan seems most convenient, and in order to avoid confusion it is proposed that the resulting tubes should be called "tubes of polarization," while the smaller tubes retain the name "tubes of induction." The polarization, as defined by J. J. Thomson in his 'Recent Researches in Electricity and Magnetism,' is measured by the number of these polarization tubes which pass through a square centimetre perpendicular to their direction.

Using Maxwell's method of drawing the boundary lines between the tubes of polarization, the equation to the n^{th} line in the case mentioned above will be

$$\frac{\frac{1}{2}l-x}{\sqrt{y^2+(\frac{1}{2}l-x)^2}}+\frac{\frac{1}{2}l+x}{\sqrt{y^2+(\frac{1}{2}l+x)^2}}=2-\frac{2n}{\mathrm{M}}, \quad . \quad (2)$$

where the straight line drawn from the positive to the negative particle is called zero, and that drawn in the opposite direction M.

4. The point of intersection of the equipotential surface V, the line of force n, and the plane of the paper lies on the curves (1) and (2). If, then, l in these equations be regarded as a variable parameter, they will together represent the curve along which the corner of an energy-cell moves, when the two particles come together. To plot this curve, the equipotential surfaces and lines of force might be drawn for a number of different distances between the particles, and corresponding points of intersection joined.

The path of the energy-cell can be obtained with less labour from measures made on a single diagram, drawn to represent the lines of force and equipotential surfaces about the two particles, when these are separated by a given distance. This is done by taking advantage of the following properties of these lines :—

1. When the distance between the particles is changed, corresponding tubes of polarization in the two diagrams are similar to one another.

2. The equipotential surfaces in the two diagrams are also similar to one another. If, however, the distance between the particles changes from l to al, the equipotential surface V changes to a similar surface, on which the potential is $\frac{V}{a}$.

If, then, the n^{th} line of force cuts the equipotential surface V at the point x, y in the first diagram, the n^{th} line will cut the equipotential surface $\frac{V}{a}$ at the point ax, ay in the second diagram.

Thus, in the case where $M=12$ and $l=10$ the coordinates of the following intersections, among others, were found by measurement on a carefully prepared diagram.

Line of force.	Equipotential surface.	x.	y.
7	1	5·15	5·95
7	4	5·35	2·28

If the diagram were enlarged in the ratio of 4 to 1, the coordinates of the point corresponding to the intersection of 7 and 4 would be $4x$ and $4y$ or 21·4 and 9·12.

The potential at this point would be $V'=\frac{V}{a}=1$.

Thus we have found the coordinates of the point of intersection of the line of force 7 and the equipotential surface 1, when the distance between the particles is 40 centim.

In the same way, and by means of the same original diagram, the point of intersection can be found for a number of other distances, and the path which it follows, when the two particles approach one another, can be plotted as in fig. 1.

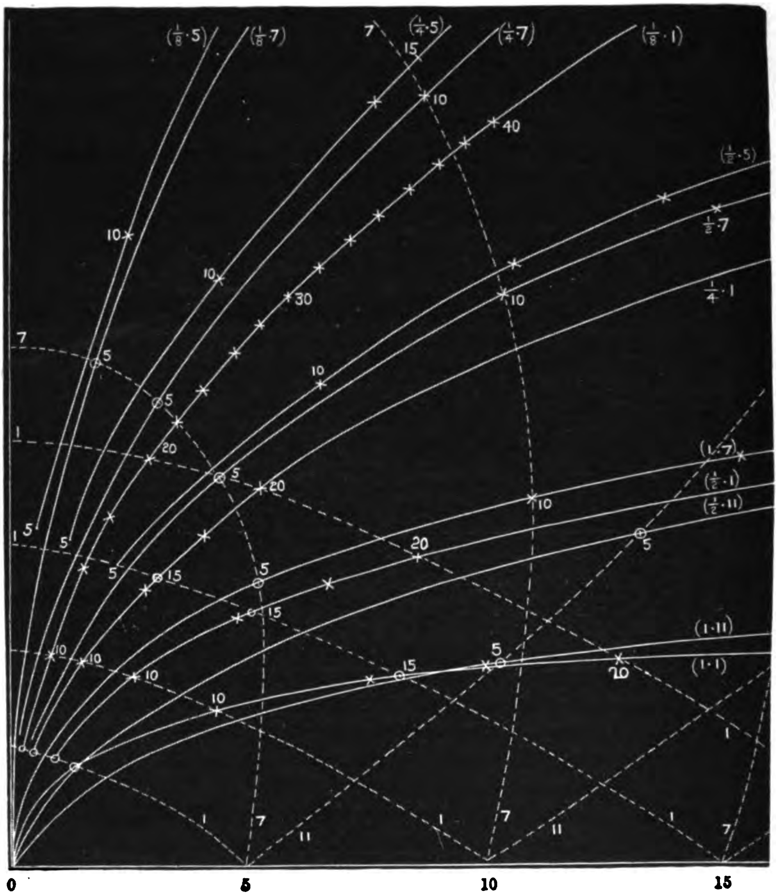
In this figure the first of the numbers in brackets attached to each curve gives the number of the equipotential surface, and the second that of the intersecting line of force. The numbers along the curves show the distance of the particles from the centre of gravity, when the energy-cell is at the point marked on the curve.

It will be seen that the energy-cells move in more or less parabolic curves towards the centre of gravity of the two particles, and that during this process they are constantly approaching the two particles; so that, if these are not infinitely small, energy must be constantly passing into them from the æther.

Maxwell has shown that in all cases the number of energy-cells in the æther is twice the potential energy of the system. So that, if we suppose each cell to contain half a unit of energy, we may regard them as preserving their identity when the bodies approach, and as being absorbed by the moving bodies, so that their potential energy is converted into kinetic. A conductor moves in such a way that the absorbed energy is a maximum.

Fig. 1 also illustrates the rotation of the energy-cell as the particles approach. If on any one of the energy-paths, as

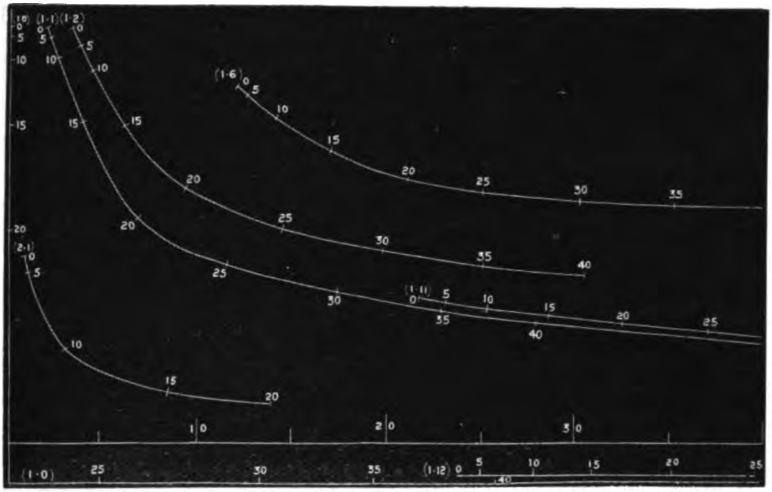
Fig. 1.



for instance $(\frac{1}{2}\,.\,7)$, the direction of the line of force (indicated by a dotted line) cutting it at different points be noticed, it will be seen that this direction constantly changes as the particles approach, so that the tangent to the line of force rotates about the point of intersection. The velocity of the different energy-cells is indicated by crosses along the curves, at such points that, when the two particles come together from an infinite distance apart, the cells move from cross to cross in equal intervals of time. The same time is taken in moving from the cross marked 10 to the origin.

5. In fig. 2 the paths of the energy-cells are shown when two equal like particles repel one another. It will be noticed that, as the particles move apart, the energy in each half of the field follows the motion of the particle in that half, and at the same time moves nearer to the central line.

Fig. 2.



It is clear that the result will be that energy will flow from the dielectric into the particle as it moves away, and being lost as potential energy will reappear as energy of motion. Even when the particles are an infinite distance apart there will still be a number of energy-cells in the æther, that is, the particles will still possess potential energy.

This is explained by supposing that every polarization tube must begin and end somewhere. In this case we may suppose that though A and B are an infinite distance apart, the negative particle C is again an infinite distance beyond A, and the negative particle D an infinite distance beyond B, so that the tubes from A end in C, and those from B in D. Then, after B and A have been repelled to a great distance from one another and all the potential energy due to their original nearness has been exhausted, there will still remain the energy due to the separation of D from B and of A from C.

6. If H_e is the intensity of the electrostatic field, or the force acting upon a particle with unit charge;
B_e the number of tubes of induction per sq. centim., or the induction in the direction of the line of force;
D_e the number of polarization tubes per sq. centim., or the polarization or displacement in the same direction;
K the dielectric constant of the medium;

we have $H_e = \frac{B_e}{K}$, $D_e = \frac{KH_e}{4\pi} = \frac{B_e}{4\pi}$.

The length of an energy-cell is $\frac{1}{H_e}$ or $\frac{K}{4\pi D_e}$.

The area of section of the cell is $\frac{1}{D_e}$.

Thus the volume of the cell is $\frac{K}{4\pi D_e^2}$.

The energy-density is $\frac{2\pi D_e^2}{K} = \frac{B_e^2}{8\pi K} = \frac{KH_e^2}{8\pi}$.

The volume of an energy-cell is proportional to the square of its length measured along a line of force. Figs. 1 and 2 show how in general the portion of the line of force intercepted between two equipotential surfaces diminishes as the movement proceeds. The volume of the energy-cell constantly tends to diminish, though in some cases, as in fig. 2, the volume of some of the cells has to increase for a while to allow the rest to contract. During this contraction the length of the cell bears to its area the constant ratio $\frac{K}{4\pi}$.

It has seemed worth while to trace roughly the curves of equal energy-density in the æther about equal unlike and equal like particles. These are shown in figs 3 and 4. The numbers apply to masses of 100 with a distance 10 between them.

7. Maxwell has discussed (Scientific Papers, vol. i. pp. 570–571) the modifications which must be made in the theory to make it fit in with the observed facts of gravitation.

The energy diagram for two gravitational particles is the same as that for two like electrified particles. The polarization tubes go off to infinity, and do not, as far as we know, end on negative gravitational matter.

The properties of the cells between the polarization tubes and the equipotential surfaces are exactly opposite in the two cases of electricity and gravitation.

The electrical energy-cells are constantly tending to contract both in length and section, but so that the area of the section always bears a constant ratio to the length of the cell. The gravitational energy-cells, on the other hand, constantly tend to expand, the same ratio holding between area and length as in the former case. While each electrical cell contains according to Maxwell's theory half a unit of energy, the gravitational cells must be supposed to contain half a unit less of energy than the same volume of undisturbed

Fig. 3.

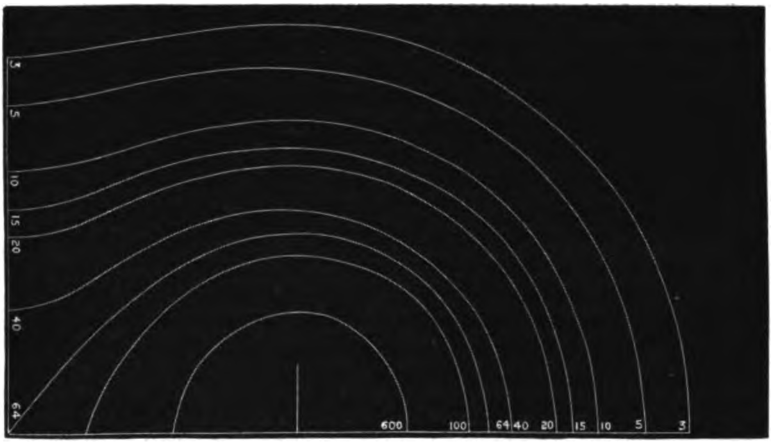
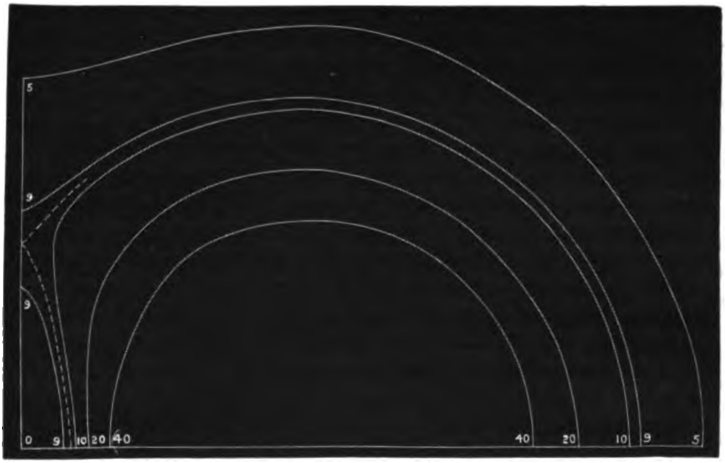


Fig. 4.



æther. The gravitational cells are negative energy-cells. This expansion of the negative energy-cells implies a kind of contraction of the energy of the gravitational æther. In the case of electricity the final state is reached when the energy-density is everywhere zero, all the energy having passed into the particles; in the case of gravitation when the density is uniform over a series of concentric shells, being a maximum at an infinite distance from ponderable matter.

8. Fig. 2 shows the path of the negative energy-cells, when two equal gravitational particles come together from an infinite distance apart. It can be seen that the cells retreat from the particles as these approach one another. There will be a greater number of negative cells in the æther when the particles are in contact than when they are at a distance. This is merely another way of saying that (positive) energy has passed from the æther into the particles.

The instantaneous position of the lines of energy-flow, for a given position of the moving gravitational particles, is something like fig. 2, the motion being away from the median plane and towards the line joining the two particles. The flow of energy is on the whole in the direction opposite to the motion of the particle. The potential energy absorbed by two gravitational particles, when they fall together, comes from the space between them.

The increase in the number of negative energy-cells, when two gravitating masses approach, is equal to twice the gain in kinetic, or loss in potential energy. The proof is the same as in the case of static electricity, due regard being paid to the signs of the quantities involved.

Thus the theory may be advanced that each of these negative energy-cells contains half a unit less of energy than the same volume of æther in which no such cells exist. An increase in number of these cells corresponds to a flow of energy from the gravitational æther into matter, where it is converted into kinetic energy.

Some difficulty may arise in special cases on account of the fact that in the case of gravitation the attracting mass has a volume distribution, instead of being confined to a surface like static electricity on a conductor. Each unit mass sends out a tube of polarization, whether it is on the surface or not, and a considerable proportion of the energy-cells exist inside the surface.

In the case of a single homogeneous sphere, at a distance from all other bodies, one sixth of the negative energy-cells are within the surface.

It is clear, then, that in general the energy is not removed from the æther at the instant the negative cell passes out through the surface, but perhaps rather at the instant that it comes out from the molecule. In other words, energy may be regarded as flowing in through the surface, but is only absorbed and converted into kinetic energy when it passes into a molecule.

9. Maxwell has calculated the enormous pressure along the lines of force and the equal tension at right angles to them required, according to his theory, to account for the attraction of the earth by the sun. A minimum value for the amount of energy in one cubic centimetre of gravitational æther can be calculated by finding the negative energy-density on the surface of the sun considered as a body of uniform density.

The volume of the energy-cells at any point is $\frac{4\pi}{H_e^2}$.

The intensity of the gravitational field on the surface of the sun is $H_e = \frac{M}{r^2}$, where M is the mass and r the radius of this body. If ρ is the density of the sun the volume of an energy-cell is

$$\frac{4\pi r^4}{M^2} = \frac{4\pi r^4}{(\frac{4}{3}\pi\rho r^3)^2} = \frac{9}{4\pi\rho^2 r^2}.$$

The amount of energy lacking in each of these cells is half a unit. Hence one cubic centimetre of æther lacks $\frac{2}{9}\pi\rho^2 r^2$ units. These are static units of energy. One dyne equals $1{\cdot}544 \times 10^7$ static units of force, therefore one erg equals $1{\cdot}544 \times 10^7$ static units of energy. Take r as $6370000 \times 100 \times 110$ centim. and ρ as $1{\cdot}39$. Then the density of negative energy at the surface of the sun will be

$$\frac{2}{9}\,\frac{\pi \times 1{\cdot}39^2 \times 637^2 \times 110^2 \times 10^{12}}{1{\cdot}544 \times 10^7} \text{ ergs per c.c.}$$

$$= 4{\cdot}289 \times 10^{14} \text{ ergs per c.c.}$$
$$= 42{\cdot}89 \times 10^6 \text{ joules per c.c.}$$
$$= 16 \text{ horse-power hours per c.c.}$$

This would seem to mean that, at a distance from all gravitating matter, a cubic centimetre of æther contains at least this amount of energy.

10. That the theory may require an even greater energy-density than this is seen as follows. Suppose the energy of the gravitational æther to be due to vortex filaments or tubes of directed energy interlacing in every direction. Take at any point three axes at right angles to one another.

The irregular distribution can be replaced in imagination by six equal sets of filaments parallel to the positive and negative directions of these three axes.

In space at a great distance from gravitational matter each of these sets of filaments will contain the same amount of energy. Let $6a$ be the amount of energy in one cubic centimetre of free æther. Let the positive direction of the X-axis at a point correspond with the positive direction of the gravitational line of force at that point. Let b be the volume of the gravitational energy-cell. Then five sets of filaments in the cell may contain $5ab$ units of energy, and the sixth, which has the direction of the X-axis, $ab-1$ units. Altogether the cell will contain $6ab-1$ units, while the same volume at a distance from gravitational matter will contain $6ab$ units of energy.

This would require the existence of 96 or say 100 horse-power hours in every cubic centimetre.

11. It is an interesting question whether this theory of energy-distribution in gravitational æther is or is not the simplest and most probable. That other distributions are conceivable appears evident. For example, the æther along the straight line joining the centres of two bodies might be regarded as a stretched elastic cord, the laws of contraction being of course quite different from those which hold for ordinary elastic bodies.

Another explanation which seems possible in the case of two gravitational particles is as follows. In the energy diagram for two equal electrified particles with opposite sign, suppose each infinitesimal tube of polarization to be divided into two equal tubes with opposite directions. If they are regarded as vortex filaments, each vortex will work in with its neighbours rotating the other way, like one friction-pulley on another.

Then it is clear that there is no way in which we can regard the two particles as opposed in sign, and yet if each of the two sets of vortex filaments acts as electrostatic tubes always act, the particles will be attracted together.

The energy-flow in this case will be as indicated in fig. 1, and the distribution of energy-density as in fig. 3. It has not been found possible to map the energy field in this manner for three or more particles. Indeed, the difficulties are such that it seems improbable that this method can be applied.

12. In conclusion it may be well to notice again the assumption on which this paper is based: that the energy-cells preserve their identity, and carry the same energy with them throughout their path. It is not clear that this is necessarily

true. It may be that energy passes from the potential into the kinetic form in the æther itself, and not merely on the surface of the molecules. Kinetic energy may consist of the motion of the whole system of energy-cells. This would lead us very near the theory which regards the molecule as being nothing but the mathematical centre from which forces proceed, or perhaps, from another point of view, as having infinite extension.

XXXV. *On a Simple Form of Harmonic Analyser.* By GEORGE UDNY YULE, *Demonstrator in Applied Mathematics, University College, London* [*].

> "The subject of the decomposition of an arbitrary function into the sum of functions of special types has many fascinations. No student of mathematical physics, if he possess any soul at all, can fail to recognize the poetry that pervades this branch of mathematics."—OLIVER HEAVISIDE.

§ 1. ABOUT a year ago several instruments for determining the coefficients of a Fourier Series expressing the equation to a given curve were described before this Society by Professor Henrici [†]. One of them, Professor Henrici's shifting-table analyser, used a planimeter as the integrator; an arrangement that seemed to me very noteworthy from the point of view of simplicity and cheapness. The analyser I am going to describe also uses a planimeter: consequently it can also only give the value of one coefficient at a time.

§ 2. Let P Q R be the curve to be analysed. Let the base P R range from $x=-l$ to $x=+l$, and the equation to the curve in terms of a Fourier Series be

$$y=\tfrac{1}{2}A_0+A_1\cos\theta+A_2\cos 2\theta+\dots$$
$$+B_1\sin\theta+B_2\sin 2\theta+\dots,$$

where

$$\theta=\pi x/l$$

and $\tfrac{1}{2}A_0$ is the mean ordinate of the curve. The values of the other coefficients are given by

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[*] Communicated by the Physical Society: read March 8, 1895.

[†] Phil. Mag. xxxviii., July 1894; also Catalogue of the Mathematical Exhibition at Munich (1892-93).

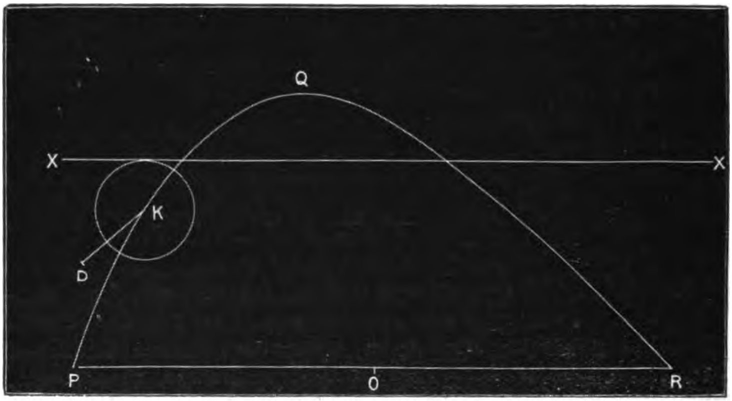
$$A_n = \frac{1}{l}\int_{-l}^{+l} y \cos n\theta \, d\theta,$$

$$B_n = \frac{1}{l}\int_{-l}^{+l} y \sin n\theta \, d\theta.$$

These are the integrals which any harmonic analyser has to evaluate.

Now suppose we have a circular disk, centre K (fig. 1), constrained to keep in contact with a straight line X X parallel to P R, and capable of rolling along X X without slip. Further, let X X be capable of motion in the plane in a vertical but not a horizontal direction, so that every point fixed in it describes a perpendicular to P R. Then we can make the point K trace out any arbitrary curve by moving X X and rolling the disk along it.

Fig. 1.



Bring K over P, and then mark any point D on the horizontal diameter at a distance r from the centre (not necessarily inside the disk). Starting from P carry K right round P Q R and back to P again by the motion just described. Supposing the circumference of the disk to be an aliquot part of P R, say $2l/n$, let us find the area of the curve traced out by D during this operation. As the disk turns through an angle $2n\pi$ in rolling along a length $2l$ of X X, it will turn through $n\pi x/l$ in a distance x; so if x, y be the coordinates of K at some point on its journey, the corresponding coordinates of D will be

$$x - r \, . \cos n\pi \, . \cos n\theta,$$

$$y + r \, . \cos n\pi \, . \sin n\theta,$$

where, to fix the sign, we have assumed D to lie initially to the left of K and X X to lie above the disk, as in the figure.

Hence the area traced out by D is

$$R_1 = \int y dx - r \cdot \cos n\pi \int y\, d\,(\cos n\theta)$$
$$+ r \cdot \cos n\pi \int \sin n\theta\, dx - r^2 \int \sin n\theta\, d\,(\cos n\theta).$$

The last two integrals vanish on taking them round a closed curve. Nothing is added to either of the first two by continuing the integration from R back to P, as y is then zero. Therefore, calling the area of the whole curve P Q R α, we have

$$R_1 = \alpha + \cos n\pi \cdot \frac{rn\pi}{l} \int_{-l}^{+l} y \sin n\theta \cdot dx.$$

Similarly, if D had been initially on the vertical instead of on the horizontal diameter, and below K, we should have had

$$R_2 = \alpha + \cos n\pi \cdot \frac{rn\pi}{l} \int_{-l}^{+l} y \cos n\theta \cdot dx.$$

It will evidently be convenient to take r some multiple of $1/\pi$ units of length, say 10. We then have, rewriting the last two equations,

when $r = 10/\pi$

$$R_1 = \alpha + \cos n\pi \cdot 10 n B_n, \quad \ldots\ldots \quad (1)$$

$$R_2 = \alpha + \cos n\pi \cdot 10 n A_n. \quad \ldots\ldots \quad (2)$$

Care must be taken with regard to the sign on the right-hand side if any other initial position of disk and line be assumed than that dealt with above.

§ 3. These two equations contain the whole theory of my instrument; they show how to construct a curve the area of which gives the required coefficients. The geometrical mechanism seems to me to be somewhat interesting, and to be possibly capable of generalization by the use of noncircular disks.

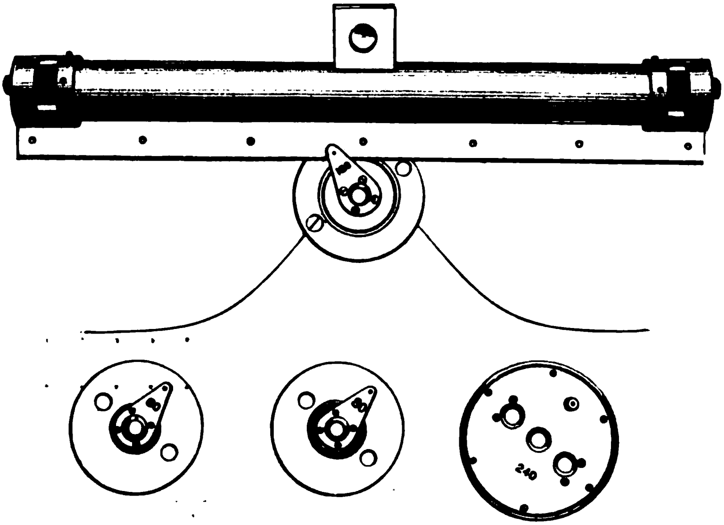
The area of the D-curve (in dealing with a material instrument) might be obtained in two ways. We might put a pencil through the disk at D, draw the curve, and integrate it afterwards: or we might attach the pointer of an integrator to D and let the integrating go on simultaneously with the following of the curve.

It is the latter alternative that I have adopted. The former method would have some advantages, but would be slow and would lead to mechanical difficulties.

§ 4. The first analyser on this principle was made for me last summer by Mr. James Hicks. Though suffering from sundry defects (due entirely to my own design) it proved a really useful and workable analyser, but required too much care and patience in use. The construction has now been entirely revised. The present instrument, designed by Mr. Horace Darwin and made by the Cambridge Scientific Instrument Company, is the final outcome. For several suggestions I am indebted to Professor Karl Pearson.

The ruler X X of fig. 1 is a rolling parallel ruler with a rack cut along its front edge (fig. 2). The weight of the rack is counterbalanced by a block projecting from the back of the rule. Normally this block swings just clear of the paper, but it may be held down when one wants to keep the ruler still.

Fig. 2.



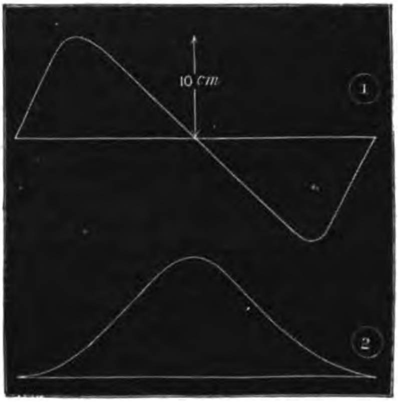
Corresponding to the disk of fig. 1 we have a series of toothed wheels; the number of teeth in the successive sizes being 240, 120, 80, and so on. Four of these disks have actually been made; they would probably be workable up to the sixth. The analyser is intended to work to a base-length of 30 centim.; the rack being cut 8 teeth to a centimetre. The ruler itself is made longer for the sake of stability.

The largest disk is the simplest. It is a flat disk of brass with teeth cut round the edge. Three windows are cut through it. One, in the centre, is glazed, and the centre of the glass is marked (on the side next the paper) with a black dot, the "tracing dot." The two remaining windows are provided with reference marks that give with the centre dot a base-line for setting the disk in any desired position. A small conical hole is made in the top of the disk, on a radius perpendicular to its base-line at a distance $10/\pi$ centimetres from the centre. This hole serves to receive the tracing-point of an ordinary Amsler planimeter, which performs the integration. The smaller disks are built up in three layers—a flat bottom plate, the toothed wheel, and a projecting crank, in the top of which is the planimeter hole. This hole is outside the circumference of the toothed wheel, so a crank or some such device is necessary. The crank swings clear above the rack when the wheel is in gear. The windows are arranged as in the first disk.

§ 5. The ordinary pattern Amsler planimeter with an arm about 16 centim. long does very well, but the tracer must be made vertically adjustable. The alteration is easily made without risk of damage. The planimeter remains of course available for its ordinary purposes, and for the determination of the absolute term.

The travel of the ruler is limited in two ways: first by the "reach" of the planimeter, secondly by the risk of running the reading wheel into the rack. Curves to be analysed must consequently be drawn to a moderate scale, but the permissible magnitude varies with the type of curve. If the type be anything like (1) of fig. 3 (sine type), 10 centim. amplitudes can be taken in comfortably; but if the type be that of (2) in the same figure, a considerably smaller scale

Fig. 3.



must be used. In cases of physical curves (*e.g.* E.M.F. curves of alternators, conduction-of-heat curves) one is generally free to choose the limits of the period so as to bring the curve to the desired type.

The accuracy of the instrument will be measured by the accuracy of the planimeter. This cannot be fairly stated in percentages, as an error of unity in the vernier reading is never difficult, and may be anything per cent. in a small total. I strongly recommend drawing curves on cardboard; it is much more favourable to the planimeter than drawing-paper. The following tests may be taken as typical of the results that are obtained with care: the curves were drawn on card:—

(1) Actual curve,

$$3{\cdot}13+4{\cdot}60\cos\theta+1{\cdot}82\cos 2\theta+{\cdot}39\cos 3\theta+{\cdot}045\cos 4\theta.$$

Analyser,

$$3{\cdot}14+4{\cdot}58\cos\theta+1{\cdot}84\cos 2\theta+{\cdot}39\cos 3\theta+{\cdot}042\cos 4\theta.$$

(2) Actual curve (sloping straight line),

$$6{\cdot}37\sin\theta-3{\cdot}18\sin 2\theta+2{\cdot}12\sin 3\theta-1{\cdot}59\sin 4\theta.$$

Analyser,

$$6{\cdot}39\sin\theta-3{\cdot}20\sin 2\theta+2{\cdot}11\sin 3\theta-1{\cdot}58\sin 4\theta.$$

The units are centimetres.

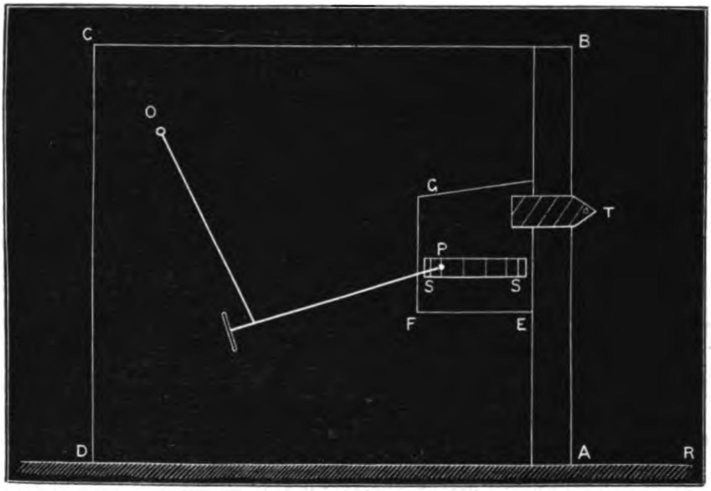
§ 6. So much for the accuracy and range of the instrument.

To get any desired coefficient, the ruler is set with its edge parallel to the curve-base and with the proper disk in gear. Ruler and disk are then adjusted till the tracing-dot stands over the point P (fig. 1), and the base-line of the disk is either vertical or horizontal according as a sine or cosine term is wanted. The planimeter-point is finally dropped into the hole provided for it, and the tracing-dot carried completely round the curve. The resulting planimeter reading will be the area of the curve plus or minus $10\,n$ times the desired coefficient.

Both hands must be used in guiding the disk, as rack and disk have to be held together while the latter is turned. The operator forms, in fact, an essential link of our mechanism which without him is unconstrained. It is this liberal use of the operator that enables me to dispense with slides, carriages, and other expensive things, and thus gain in simplicity.

§ 7. This analyser arose from a simple form of step-by-step integrator or "adder" which may be worth a brief description. The instrument is shown diagrammatically in fig. 4: it was made from materials at hand and I describe it as made. A B C D is a square sheet of card with a foot-rule glued along one edge A B. A set square F E G can be slid up and down along this rule: it is provided with a tracer T and some scales of sines S S. The whole sheet of card is guided parallel to

Fig. 4.



the axis of x by a T-square D A R clamped to the drawing-board: if the card is pulled forward by the corner A the friction keeps it set against the square. O P is a planimeter with its pole fixed to the card and its pointer P resting on one of the scales of sines, which must stand parallel to the axis of x.

Mark off along the base of the curve to be analysed a number of equal divisions, *e. g.* 6° each, and erect the ordinates y_1, y_2, &c. at the centres of each of these elements. Suppose the pointer P of the planimeter to rest initially at the zero of the scale, and the tracer T attached to the set square to stand over the origin of the curve. Pull the card forward, carry T to the top of y_1, and then shift P to 6° on the scale. Pull the card forward again, carry T to the top of y_2, and then shift P to 12°. Continue this procedure right on to the end of the curve.

P will then have come back to its starting-point on the scale, after describing on the card a certain curve or stepped polygon. The area of the polygon is

$$\begin{aligned} & y_1 (\sin 6° - \sin 0°), \\ & + y_2 (\sin 12° - \sin 6°), \\ & + y_3 (\sin 18° - \sin 12°), \\ & + \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \\ & + y_4 (\sin 360° - \sin 354°), \end{aligned}$$

a quantity which (as the elements are small) approximates to

$$\int_0^{2\pi} y\, d(\sin\theta).$$

Thus the planimeter-reading after this procedure gives us the first cosine coefficient. I need not enter at length into the mode of getting the others. For the second coefficient one would have to shift the tracer P 12° at a time instead of 6°, and so on.

In my case I actually used steps of 6°, as above; and there were three scales on E F G going by steps of 6°, 12°, and 18° respectively for the first three terms, the separation of the scales helping to avoid confusion. The results were good: for example, in one test the actual coefficients were 4·82, 1·09, ·009: the instrument gave 4·86, 1·08, ·01. The chief objection to such a non-automatic integrator is of course that one is liable to forget to shift the planimeter pointer at some stage of the proceedings. The chief advantage is that your curve need not be drawn to any particular base-length. Whatever the base, it is only necessary to divide it into the proper number of equal parts, and erect the ordinates at the centres of these elements.

Suppose we wished to make the arrangement automatic. We might substitute for the harmonic motion of P along S S a circular motion round the centre of S S. This merely amounts to giving P another harmonic motion (perpendicular to S S), a proceeding which adds nothing to the planimeter-reading if the integration be continued completely round the curve.

But this is not an easy motion to obtain mechanically. The difficulty is obviated at once if we remove the card A B C D altogether and fix the pole of the planimeter in the drawing-board. If we give P the same circular motion as before we have the "disk" analyser, which I described in the first part of this paper. The area of the curve analysed is added to the integral given by the planimeter, but that is all.

Evidently in the instrument of fig. 4 we have only taken a special case in making the scales scales of sines. We might have used scales graduated proportionally to x^n and got moments. Any other integral could be obtained approximately if a proper scale could be drawn.

XXXVI. *The Clark Cell when producing a Current.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,

IN the Philosophical Magazine for March 1895 you have published a letter from Professor Threlfall criticising my experiments on the Clark cell when producing a current. I should like to reply to some points in it.

Professor Threlfall quotes my definition of the quantity which I have called the polarization of the cell. The method of determining this quantity depended on measuring separately the resistance of the contents of the cell treated as an electrolyte and of the wire through which the cell was used to maintain a current. Knowing the current, I calculated the E.M.F. required to maintain it in an equivalent wholly metallic circuit having a resistance equal to the sum of these two values. The difference between this E.M.F. and that of the cell at rest I tabulated as the polarization with varying current-density. This point was considered very carefully by me at the time, and it appeared that the resistance of the contents of the cell could only be changed through unequal migration of ions and electrolytic endosmose. Now the effect of these two causes would be permanent when the cell was again placed on open circuit; and so if measurements taken before and after the cell was used did not show any wide divergence, it is legitimate to assume that whilst the current was flowing the resistance would lie somewhere between these two values. This is the reason which led me to adopt this method of statement of results.

The actual measurement of the resistance of the cell showed, as I expected, very little change. The testing-current was of the order of ·007 ampere.

The temperature of the 147 ohm wire through which the current of approximately ·01 ampere was maintained could not have been far different from that of the oil-bath. A current of this magnitude would only produce 12·6 gram Centigrade thermal units in one hour; and as the wire (20 grams) was openly wound "on an ebonite *frame*," it does not seem likely that it would have been much hotter than the oil. It would require a rise of 10° C. to produce a change of ·6 ohm. The case is not at all comparable with Mr. Griffiths', where current up to an ampere was used. Besides, it must be remembered that any possible error in the resistance of this wire would have very little influence on the magnitude of the quantity which I have called the polarization of the cell.

My results when the current was maintained indicate that the potential-difference at the electrodes became less. In my earliest experiments, when two Leclanché cells were used in the potentiometer circuit, I found an effect similar to that observed by Professor Threlfall. This is stated in my paper, § 5 and § 7, and as such a result was not expected and did not for many reasons seem to be connected with the Clark cell, I placed large Clark cells in the place of the Leclanchés.

The considerations which led me to make this change may be shortly summarized. Firstly, the comparison of the size of the plates in the two cells is greatly in favour of the large Clark, and also the soluble depolarizer in that cell would cause more efficient depolarization. Secondly, I have frequently observed when using the potentiometer that the same value may be obtained for the potential-difference of a short-circuited Clark before and after an interval during which the Clark has been on open circuit, provided no large plug change has been made during the interval. On the other hand, a large plug change, such as testing the E.M.F. of the cell with its poles open will lead to a new value when its poles are again closed. Thirdly, when determining the absolute value of the E.M.F. of the Clark cell with Mr. Glazebrook (Phil. Trans. 1892), we thought it safer to avoid large plug alterations, and so abandoned this process to adopt one in which a mercurial rheostat in the main circuit could be varied so as to maintain the electrodes of the standard resistance at a constant difference of potential. With this alteration my experiments became regular; seven sets were obtained (one lasted 16 hours), and I was satisfied that the original irregularity was due to the Leclanchés. The average of four sets is given in my paper. If I were to repeat these measurements I should now use one large accumulator and a wire rheostat for that part of the potentiometer where alterations of resistance would have to be made, and thus avoid all rapid plug changes. This arrangement would, I am sure, give better results.

My object in referring to Mr. Fitzpatrick's paper in the easily accessible B.A. Reports was to avoid a lengthy description of an apparatus which is in continuous use in the Cavendish Laboratory. In his paper Mr. Fitzpatrick has made the proper references to Macgregor's and Professor Kohlrausch's well-known work.

I am, Gentlemen,
Yours respectfully,
S. Skinner.

Cambridge, March 9, 1895.

XXXVII. *On some Experiments with Alternating Currents.* *By* A. Sadowsky, *University Professor in Turiew (Dorpat), Russia*[*].

To the Editors of the Philosophical Magazine.

Gentlemen,

In No. 238 (vol. xxxix. 1895) of your valuable Magazine Mr. Griffiths has published a paper on "Some Experiments with Alternating Currents," in which he describes some experiments with Lenard's bismuth spiral. I was investigating the same subject in 1892–1893, and obtained the following results, agreeing well with those of Mr. Griffiths.

(1) With the bismuth spiral in a strong field absolute silence in the telephone is never obtained, but only a minimum of sound.

(2) The superficial distribution of alternating currents is without influence on the resistance.

(3) The resistance of bismuth depends on the phase of the current.

The following results are similar to those of Mr. Griffiths, but do not coincide with them in every respect:—

(1) The bismuth spirals have something like the self-induction, *but not equivalent* to it; I have tried the hypothesis

$$r=r_0\left(1+\frac{\lambda}{i}\frac{di}{dt}\right),$$

where r_0 is the resistance for a constant current,
i the current,
λ a constant positive coefficient, and
r apparent resistance (measured with a Wheatstone bridge and telephone).

Under this hypothesis r must be always $>r_0$, which does not agree with the experiments of Lenard, Zahn, and myself.

(2) I have observed the difference of resistance with frequency 500 without field to be as stated by Messrs. Lenard and Zahn; the resistance with a constant current was greater (0·1 per cent.).

In addition to the above, I have found the following:—

(1) M. Lenard's statement that the difference of resistance is due to the currents of great frequency, *i. e.* 10,000, is erroneous. Let ordinates of the curve A B C D represent the

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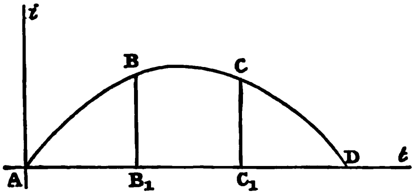
[*] Abstract of a paper published in the Journal of the Russian Physico-Chemical Society, vol. xxvi. pp. 81–156 (1894).

current and abscissæ the time. If we divide the curve in three parts AB, BC, CD, such that $AB_1 = B_1C_1 = C_1D$ (approximately), and measure the resistance with the currents

Fig. 1.



AB, BC, CD; then denoting the measured resistance by ρ_1, ρ_2, ρ_3, I have obtained experimentally:—

(*a*) Without magnetic field, with frequency 4–6:

$$\rho_1 = \rho_2 = \rho_3.$$

(*b*) With intense magnetic field, with the same frequency, 4–6:

$$\rho_1 > \rho_2 > \rho_3.$$

Taking ρ_2 as unity, the following figures are obtained for four spirals:—

ρ_1.	ρ_3.
1·0045	0·9927
1·0037	0·9938
1·0030	0·9940
1·0036	0·9943

If we take the currents represented by the curves figs. 2 and 3 and measure the same ρ_1, ρ_2, ρ_3, we obtain as above,

$$\rho_1 > \rho_2 > \rho_3;$$

but the differences $\rho_1 - \rho_2$ and $\rho_2 - \rho_3$ are much smaller than with the current ABCD.

My method of experimenting for obtaining the data for ρ_1, ρ_2, and ρ_3 was similar to that of Mr. Griffiths. The alternating current was supplied by a small magneto-electric machine set in motion by an electromotor. This current was sent through a Wheatstone bridge, in one branch of which was placed a bismuth spiral. The galvanometer branch contained an automatic double intermittent contact (rotated by the magneto-electric machine supplying the alternating current), by which it was possible to complete the circuit of the galvanometer for the parts of the current AB or BC, and BC or CD, and thus to compare immediately ρ_1 with ρ_2, and ρ_2 with ρ_3.

In the first part of my investigation I measured without field the resistance of a bismuth spiral with a telephone, and an alternating current obtained from a Kohlrausch inductorium. As interrupter I took a toothed wheel turned by an electromotor; the frequency of interruption varied between 92 and 2088, the difference of resistance varied with the frequency between 0·12 and 0·27 per cent.

Fig. 2.

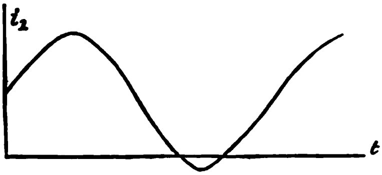
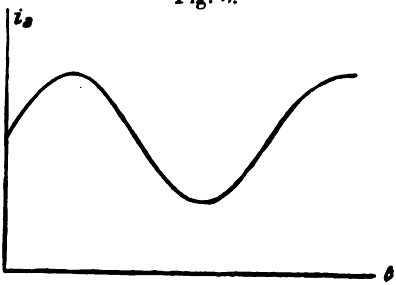


Fig. 3.



March 18, 1895.

XXXVIII. *Notices respecting New Books.*

The Great Ice Age and its Relation to the Antiquity of Man. By James Geikie, *D.C.L., LL.D., F.R.S., &c.* Third Edition. Pages i–xxviii; and 1–450; with 18 maps and 78 illustrations. 8vo. Stanford: London, 1894.

THIS new edition of an important geological work has been "largely rewritten" by the Author, and contains two new chapters on the "Glacial Phenomena of North America," by Professor T. C. Chamberlin.

As a systematic account of the visible results of ice-action on a large scale in this part of the World, and of the probable history of the origin, progress, and end of this period of glaciation, we have here a valuable repertory of facts and opinions recorded by many geological enquirers and grouped by one who has studied the subject for almost a life-time. Formerly one of the members of the Geological Survey engaged in mapping the geology of Scotland, and now holding the Chair of Geology at Edinburgh, Professor James Geikie has naturally taken up one of the most interesting groups of geological features in that country as a special study. The nature, characters, and distribution of the till (boulder-clay) and erratics, striated rock-surfaces, rock-basins, kaims and escars, beds of arctic shells, and the local alternations of sands, gravels, clays, and lignites with the till, have readily attracted the attention of geologists, and the consideration of their probable origin fully occupies the philosophic mind and feeds the scientific imagination. As similar natural features abound in other parts of the world, scientists of many sorts, having concluded that ice must have been the chief agent concerned with these phenomena, have carefully observed its various physical conditions, and have invented many hypotheses about its movements and their results. The compilation of these facts and opinions, here offered by the Author, is naturally affected by his own predilections and conscientious beliefs, which occasionally lead him to oppose or ignore some even late researches on ice-fields and superficial drifts.

The "List of Authors quoted or referred to" (about 580) at pages 832–838 indicates the wide extent of the literature to be dealt with; and Prof. J. Geikie intimates with truth that the list does not exhaust what has been published about the facts and inferences relating to glacial phenomena and the former existence of wide-spread and intense action of Ice on some parts of the Earth's surface.

In the first (1874) and second (1878) editions of this book, "The Great Ice-Age and its relation to the Antiquity of Man," Scotland supplied, as now, the typical facts and phenomena of a Glacial region, with its subsequent (Post-glacial) conditions; and, as great changes of climate seemed to be involved in that geological history, these were considered on the basis then regarded as the best available. Clearer recognition of leading facts, and their more perfect explanation, have much modified the hypotheses that were then received as good and useful; and the Author in this, the Third Edition, endeavours to give his opinion clearly on the results both of the new and extended examinations of the physical phenomena, and of many criticisms on the one hand, and helpful suggestions on the other.

In the order of the subject-matters of the book, the glacial deposits seen in Scotland come first, with the boulder-clay, its composition, relative position, special characters, and local features. Various modes of its origin, hypothetically advanced, whether by violent aqueous agency, or by the mediation of glaciers and icebergs, are dealt with; and a careful account is given of glaciers, and of the modes and results of their action on the surface of the ground.

Chapter IV. is devoted to icy Greenland and its supposed constitution of separate islands; and treats of Arctic glaciers, with icebergs, foot-ice, and sea-ice, and the littoral accumulations of earthy and stony débris. These are illustrative of much of the ice-work which has modified the surface of Scotland.

The glacial origin of the Till being accepted, there follows a consideration of the probable modes and processes of ice-action in producing its clay and stones, and in grinding, rounding, polishing, and scoring the latter (Chapters V. and VI.). Doubtless the glacier, as is well known, could do all this; but it is very doubtful indeed if the boulder-clay was a persistent floor of any glacier; or that the stones were not all derived from the frozen rocks of the valley giving off their débris from the sides to its surface. No ice could tear solid blocks from the floor. Water running beneath the glacier carries along abundant mud and sand amidst the grinding pebbles of the so-called "moraine profonde;" and, though some layers are lodged in hollows and quiet recesses, the rest passes on towards the glacier's foot, wherever that may be, in river, fiord, or open sea. These considerations, as to whether it was a persistent bed on the glacier's floor (quite impossible), or accumulated at its foot by water, with or without icebergs and ice-floes, necessarily affect the explanation of the local occurrences and disposition of the Boulder-clay, also of its recurrence after the existence of a land-surface, and of its occasional fossil shells and other organisms.

The physical evidences of ancient ice-sheets ("mers de glace") affecting Scandinavia and the British Isles, and regarded as having been more or less conterminous or continuous, are enlarged upon, and Pl. IX., opposite page 437, delineates the supposed greatest extent of this glaciation. Whether, however, this condition existed over the European area uniformly at one and the same time, and how thick the main ice-sheet may have been, are points not yet proved to the satisfaction of all. In this, as in some other cases, the Author prefers to collate and use the ideas and statements supporting his views, without reference to contrary opinions.

Stratified and unstratified beds associated with the Scottish Till form the text of Chapters VII. to XIII. At page 89 allusion is made to "gravel, sand, silt, mud, brick-clay, and peat" that underlie the lower till, and to similar beds lying upon it and covered by the upper till. Some such deposits contain freshwater fossils, and in some others there are marine shells. These "beds below and in the till" are stated (p. 192) to indicate pauses in its formation (though the lowest, being *beneath*, would seem to have been formed previously!), and to have been due to ordinary water-action. They are often of great interest, and have been carefully examined by the geologists of Scotland wherever met with in exposures, diggings, and borings. From them much has been gathered as to the probable changes of fauna and flora under different successive climates ("recurrent cold and warm periods"); also of the former varying lines of rivers and lakes, and of the conditions and features of the country during the formation of these "glacial" and "interglacial" deposits.

Chapters XIV. to XVII. treat of glacial deposits overlying the till of Scotland, and their origin. These are the åsar (escars) and kames, ridges, mounds, and terraces of gravel and sand, due to the material of moraines of probably decaying glaciers having been shifted and arranged by strong streams of water running therefrom; hence they are said to have been formed by fluvio-glacial agency. Scattered blocks ("erratic"), brought from a distance and left on the melting of the ice, and morainic accumulations left in mountain-valleys, come in the same category as the above.

Lakes and rock-basins occupy Chapters XVIII. and XIX. Several modes of origin are known for lakes, and some are briefly mentioned here. For lakes in the supposed ice-ploughed hollows in solid rock, a favourite subject with his friend the late Sir Andrew Ramsay, Prof. J. Geikie advances all the evidence he can, ignoring what has been brought forward and published to the contrary.

Chapters XX. and XXI. explain that other superficial deposits later in age than the "upper till" were brought about by the existence of "district ice-sheets and local glaciers," belonging to Dr. J. Geikie's "third glacial epoch" (p. 283). These, he thinks, succeeded "interglacial" conditions, and were locally coincident with some shelly deposits on the sea-board, especially along the Firths of the Clyde and Forth. It is to this period that the Author now refers the origin of the "parallel roads of Glenroy" by the intervention of the great western ice crossing the neighbouring valleys lower down and thereby causing lakes, as first suggested by Agassiz, and subsequently defined by Jamieson and Prestwich (p. 283).

Later formations, either within, or just subsequent to the Glacial Period are noted in Chapters XXII. & XXIII., as peat-bogs, raised beaches, sand-dunes, river-terraces, and old lake-beds, bearing recognizable evidence of their relative age, contemporary with a partial submergence of the land; and with a cold climate, destructive of the forests and giving rise to some highland glaciers. A repetition of the foregoing or similar conditions; and then the last elevation of the land, and the arrival of the present state of things, constitute part of the eleven successive changes, from the "lower till" to the existing land and sea, succinctly enumerated at page 325, so far as Scotland is concerned.

We are now led to the consideration of glacial phenomena met with (1) in England and Ireland; (2) Northern Europe; (3) Central Europe; (4) the Alps, and other parts of Europe, in Chapters XXIV. to XXXVI. This last chapter enumerating five glacial epochs, each with its interglacial epoch, brings us to present or, rather, prehistoric times, and comprises long periods during which Man has existed in this part of the World.

The last or "present" epoch (p. 612) was "marked in Britain by the retreat of the sea to its present level, and by the return of milder and drier conditions, and the final disappearance of permanent snow-fields."

The Author arranges the "glacial succession" in the British Islands as follows (beginning with the lowest):—

1. Weybourn crag and Chillesford clay. Marine deposits with pronounced arctic fauna.
2. Forest-bed of Cromer. Temperate flora; *Elephas meridionalis, E. antiquus, Rhinoceros Etruscus, Hippopotamus*, &c.
3. Lower Boulder-clays and associated fluvio-glacial deposits. Ground-moraines (?)*, &c., of most extensive ice-sheet.
4. Marine, freshwater, and terrestrial accumulations; basin of Moray Firth; basin of Irish Sea; Lanarkshire; Ayrshire; Edinburghshire, &c.; Hessle gravels; Sussex beach-deposits, &c.; Settle Cave, &c.
5. Upper Boulder-clay and associated fluvio-glacial deposits. Ground-moraine (?) of ice-sheet which extended south to the Midlands of England.
6. Freshwater alluvia underlying oldest peat-bogs; probably a considerable proportion of our so-called "post-glacial" alluvia. Temperate flora and fauna; Irish deer, red deer, *Bos primigenius*, &c.
7. Boulder-clays and terminal moraines of mountain-regions. The 100-feet beach of Scotland; arctic-plant beds. Moraine accumulations of district- and large valley-glaciers; arctic marine fauna; snow-line at 1000 to 1600 feet; arctic flora.
8. Lower buried forest. Temperate flora and fauna.
9. Peat overlying the "lower buried forest;" Carse-clay and raised beaches; valley-moraines; corrie-moraines.
10. Upper buried forest. Temperate flora and fauna.
11. Peat overlying "upper buried forest;" low-level raised beaches; high-level valley- and corrie-moraines. Small glaciers in the most elevated regions; snow-line at 3500 feet.

The contemporary European formations for each of the eleven above-mentioned epochs follow at pages 614 and 615.

In arriving at his conclusions as to the succession of the "Glacial" deposits, and as to the conditions under which they were probably formed, the Author has evidently been specially influenced by his belief that the main agents have been enormous "ice-sheets" and their supposititious "ground moraines," of great thickness and consistency; and not separate glaciers, icebergs, ice-floes, and coast-ice, making and distributing mud and sand with gravel and boulders, and helping to make up the full score of striæ. For the changes of climate accounting for the coming and going of the seemingly probable arctic and temperate conditions, indicated by the glacial and non-glacial phenomena, the Author favours the astronomical (Croll and Ball) hypothesis.

Prof. Geikie argues assiduously and plausibly on all these points, without allowing full weight to published objections. An ideal *moraine profonde*, such as would suit a widely continuous and thick "boulder-clay," would far exceed the limited dimensions and conditions of the movable mixture of mud, sand, and stones, that grind and are ground on a glacier's floor, until they find exit at the terminal moraine, or are taken off by icebergs to form submarine till. If the maxima, or even the existence, of ice-sheet periods are to be calculated according to the extent and thickness of such supposed *boulder-clay floors* (hundreds of feet thick), the calculations must be erroneous: whilst doubtless the distribution, by river, lake, and sea, of the clay and stones resulting from the grinding work of the glaciers simply and satisfactorily meets many of the geological requirements.

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* See above, p. 381, for some remarks on the *moraines profondes*, supposititious as far as the great boulder-clays are concerned.

A very large amount of instructive geological detail, obtained by personal research and from a variety of sources, is arranged systematically in treating of stratified and other formations whose origin was in any way associated with periods of extreme cold and with milder intermediate times,—for Scotland (as we have seen) in Chapters II. to XXIII.; for England in Chapters XXIV. to XXVII.; and for Ireland in Chapter XXVIII. The amount of information collected for Europe (Northern, Middle, Alpine, and Western) in Chapters XXIX. to XXXVI. is extensive, and is carefully arranged; resulting (pages 607–615) in the Author's determination of six *glacial* epochs, each with its sequent *interglacial* period; the last of the latter exists at present time.

He supports this frequency of climatal changes by reference to his interpretation of successive glacial and non-glacial deposits, and the concomitant topographical modifications in the outlines, heights, and depths of land and water. These being more numerous and complicated than they were thought to be when his earlier editions were published.

A careful study of the many published accounts of the nature, extent, and origin of the Loess or Lehm is given in Chapter XXXVIII. This Pleistocene deposit is described as a fluvio-glacial inundation-deposit, largely modified and rearranged by wind, snow, and dust-storms, and naturally containing multitudinous mammalian bones, many land-shells, and other rarer fossil remains. It necessarily constitutes an important link among the results of the dying ice-age, and the gradual disappearance of the glaciers.

The advent of a cold climate was indicated for Europe in the Pliocene times; and the *maximum* of cold occurred in the "Second Glacial Epoch." Then the alternating cold and temperate periods successively declined in importance. Palæolithic Man is regarded (p. 689) as having appeared in Europe in Pleistocene times, probably not before the "Second Interglacial Epoch" (*Elephas-antiquus* stage); and, surviving the "Third Glacial Epoch," he probably retired to Southern France, and to Switzerland and the country of the Danube.

Respecting the relative chronology of the Glacial Epoch and the appearance of European Man, it may be well to note that Dr. Croll at first suggested that the beginning of the Glacial Period may have been about 1,000,000 years ago, and that it may have lasted about 2,000,000 years; afterwards he approximately fixed the incoming of that Period at 240,000 years ago, and its termination about 160,000 years afterwards (80,000 years ago). Prof. Prestwich considers that Palæolithic Man, that is, the man of the Valley-drifts, appeared in Western Europe probably not longer ago than about 20,000 or 30,000 years, and disappeared about 10,000 or more years ago. He was probably preceded by the Plateau or Eolithic Man (referred to in the footnote at page 640), before the time of extreme glaciation; and he was certainly succeeded, with some intervening lapse of time (page 619), by the Neolithic Man.

Before taking up the subject of glacial phenomena in Asia, Australia, and North and South America, in Chapters XL. to XLII., Prof. Geikie gives two interesting chapters on Cave-deposits, Valley-drifts, and the Loess of Central Europe. The last of these has been already referred to. The first involves a consideration of the two Stone Periods (old and new), and evidences of human work and occupation in England and France. For the Valley-drifts M. Ladrière's results are given in detail, in preference to Prof. Prestwich's work; and, though the latter is not lost sight of, the treatment is one-sided (pp. 629–637), brief references being made to Prestwich's elaborate memoirs explanatory of river-gravels, and a full account given of M. Ladrière's paper illustrative of views which appear somewhat artificial. So also we should like to have seen further references to Prestwich's work and views on the Pliocene Crags and the associated Pleistocene Beds of the Eastern Counties, besides the useful notes derived from Mr. Clement Reid's excellent memoir (pp. 329–336); and, with reference (in the footnote at p. 603) to the "rubble-drift," we may observe that the Author should have remembered that Prestwich limited its range to 1000 feet *in England only*, and gave several cases where it exceeds 1500 and 2000 feet on the Continent. His name also might with advantage have been given (at p. 392) at the same time as Mr. A. Collinette's. Prof. Bonney's researches on ice-work and its results seem to have altogether escaped notice. It may be that, with the multiplicity of facts and inferences gathered for assimilation whilst preparing a voluminous work, an Author can scarcely avoid handling some subjects and some writers less carefully and judiciously than others. Prof. Geikie seems to be aware of this; and apologises in his Preface for any such inadvertencies and shortcomings.

Professor Chamberlin's two Chapters on the Glacial phenomena of North America (pages 724–775) give a concise and clear account of the enormously extensive glacial drifts covering nearly one half of the country. The great ice-field of Greenland, as now, lay formerly to the north-east; and on the mainland glaciers were formed on the high grounds of Canada and Labrador, spreading and coalescing into the great so-called Laurentide ice-sheet. On the west side of the Rocky Mountains and Cordilleras confluent glaciers were another centre for the formation and dispersion of "drift." The glacial deposits of North America, numerous, extensive, and thick, overlapping one another, reach southwards to the coast of New York and New Jersey, and over-ride the States that lie north of the Ohio and Missouri.

The till, drumlins, escars, kames, sand-plains, glacio-fluvial moraine-aprons with their valley-drifts and sheets of silt or loess, partly due to ice and water and partly to wind, are definitely handled.

One of the classifications of the great North-American drift-series suggested by Prof. Chamberlin is as follows:—

Glacial Period.

1. Concealed deposits (theoretical).
2. Kansan stage of glaciation: First Glacial Epoch.
3. First Interglacial Epoch.
4. East-Iowan Stage: Second Glacial Epoch.
5. Second Interglacial Epoch.
6. East-Wisconsin Stage: Third Glacial Epoch, perhaps comprising a Fourth Epoch.
7. Later oscillations.

Professor Geikie thinks that this arrangement is closely parallel with the glacial history which he has described for this part of our hemisphere. He regards the Kansan stage as equivalent to his own "Second Glacial Epoch," with the maximum glaciation, and specially applicable to the *Lower Diluvium* of Central Europe. The East-Iowan matches his *Third* epoch; and he finds corresponding features in Europe for the East-Wisconsin, and even for the possible fourth epoch entertained by Prof. Chamberlin (p. 775).

In the Appendix, pages 817–826 give a well digested account of the published evidences of the results of glacial action at various geological periods, in many parts of the world. Indeed it is pointed out that proofs, more or less distinct, occur in all, or nearly all, the geological formations, of contemporary glacial boulders or glaciated surfaces. The Appendix contains also an account of Loch Lomond and its map (Pl. XVI.); and remarks on the maps, Pls. I., IX., X., XI., XIII., XIV., and XV., showing the directions of glaciation in the British Isles, Europe, Asia, and North America. Notes on the map, Pl. XII., showing the distribution of land and sea in Northern Europe after the last great Baltic glacier come also in this Appendix, p. 832. Eight other maps and charts are given in the volume; and 78 woodcuts of views, sections, rocks, and illustrative diagrams are scattered through the text.

A General Index and one of Authors are useful adjuncts to this elaborate history of the "Great Ice Age."

XXXIX. *Intelligence and Miscellaneous Articles.*

SILVERING GLASS IN THE COLD.

BY MM. AUGUSTE AND LOUIS LUMIÈRE.

FOR silvering glass in the cold, a number of methods have been described which appear open to the objection of being very complicated, and of requiring very minute precautions.

In investigating the properties of formic aldehyde, we have observed that this substance gives with ammoniacal solutions of silver nitrate, adherent mirrors which can be readily polished. By working under suitable conditions, we have observed that the greater part of the silver contained in the solutions is deposited on the glass, thus avoiding residues and diminishing the cost.

After numerous trials we have arrived at the following method.

100 cubic centim. are taken of a 10-per cent. solution of silver nitrate to which ammonia is added drop by drop, so as just to redissolve the precipitate formed at first. Care must be taken to avoid an excess of ammonia, which would hinder the formation of the deposit. The volume of the solution is made up to a litre by distilled water, and we thus obtain what we shall call A.

On the other hand, commercial formaldehyde of 40 per cent. is diluted with distilled water so as to form a 1-per cent solution. Owing to its dilution this solution, B, may be kept for some time.

The surface of the glass is carefully polished by rubbing it with chamois covered with rouge, and two volumes of A are rapidly mixed with one volume of B, and the mixture is rapidly poured over the glass to be coated.

In five or six minutes, at the temperature of 15° to 19°, all the silver in the solution is deposited in a brilliant layer which is washed with water. It is then dried, and varnished if the surface in contact with the glass is to be the reflecting surface, or polished with the ordinary precautions where the layer itself is to be used as in astronomical instruments.—*Journal de Physique*, January 1895.

ON THE GLOW-DISCHARGE. BY A. HERZ.

The results of this research are summed up by the author as follows:—

1. The potential gradient v in the positive unstratified glow-light with constant current diminishes as the current i increases, and the value of this decrease is given with sufficient accuracy by the equation

$$v=v_0-b(i-i_0).$$

The value b, that is the decrease of the gradients for unit increase of the current strength, decreases as the width of the tube in the clear increases, and for the same width has almost the same value for nitrogen and for hydrogen.

2. The potential gradient in question decreases as the clear width of the tube increases; and

3. Increases as the pressure increases, but more slowly than in proportion to the pressure.

4. For nitrogen quite free from oxygen it is, for pressures between 4 and 8 mm., 1·4 times as much as hydrogen.

5. A small admixture of oxygen with the nitrogen increases it; a small admixture of aqueous vapour with nitrogen produces no change.—Wiedemann's *Annalen*, No. 2, 1895.

PRIZE-QUESTION PROPOSED BY THE SCHNYDER VON WARTENSEE'S FOUNDATION FOR ARTS AND SCIENCES, ZÜRICH.

The Schnyder von Wartensee's Foundation again proposes for the year 1897 the following prize-question on problems in Physics.

"As the numbers which represent the atomic heats of the elements still show very considerable divergences, the researches conducted by Professor H. F. Weber on boron, silicon, and carbon, on the increase of the specific heat with the temperature, are to be extended to several other elements prepared as pure as possible, and also to combinations or alloys of them. The densities and the coefficients of thermal expansion of the substances investigated are further to be determined as accurately as possible."

The conditions are as follows:—

Art. 1. The treatises handed in by competitors for the prize-question may be either in German, French, or English, and must be sent in by September 30th, 1897, at the latest, to the address given in Art. 6.

Art. 2. The examination of the treatises will be entrusted to a jury composed of the following gentlemen:—

Professor Pernet, Zürich.
„ A. Hantzsch, Würzburg.
„ E. Dorn, Halle-on-the-Saale.
„ J. Wislicenus, Leipsic.
„ G. Lunge, Zürich, as member of the committee proposing the prize-question.

Art. 3. The Prize Committee has at its disposal a sum of four thousand five hundred francs, of which a first prize, of no less than three thousand francs, will be awarded and minor prizes for the remaining sum.

Art. 4. The work to which the first prize is awarded remains the property of Schnyder von Wartensee's Foundation, which has to arrange with the author regarding its publication.

Art. 5. Every treatise sent in must bear a motto on the title-page and be accompanied with a sealed envelope containing the author's name and bearing the same motto outside.

Art. 6. The treatises are to be sent to the following address, within the period named in Art. 1:—

"An das Präsidium des Conventes der Stadtbibliothek in Zürich (concerning prize-question of Schnyder von Wartensee's Foundation for the year 1897)."

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[FIFTH SERIES.]

MAY 1895.

XL. *Tests of Glow-Lamps, and Description of the Measuring Instruments Employed.* *By* Prof. W. E. AYRTON, *F.R.S.*, *and* E. A. MEDLEY[*].

THE conditions under which the glow-lamp can be most economically used have attracted considerable attention since a paper entitled "The Most Economical Potential Difference to employ with Incandescent Lamps" was read before the Physical Society in February 1885[†] by Professor Perry and one of the authors of the present communication. In this paper they stated that it was well known, from experiments made by their students in 1880, and from results published in 1881 by Lord Kelvin, then Sir William Thomson, as well as from subsequent experiments, that the light obtained from an incandescent lamp increased much more rapidly than the power expended in it; or, that the number of candles produced per watt of power expended in the lamp increased as the filament became hotter. But it was pointed out in the paper in question that such experiments by themselves gave no idea of the commercial value of any particular glow-lamp, because they afforded no indication of its life when run at different efficiencies, and it was known that the length of time a filament would last was the less the higher its temperature.

They then proceeded to show that the cost of lighting per hour per candle could be divided into two parts, viz., the cost as to lamp renewals and the cost as to power, the first being equal to the price of a lamp divided by the product of its life into its candle-power, and the second to the price of one watt-hour multiplied by the watts per candle. So that, if L(v), C(v), and W(v) were the life in hours, the candle-power, and the watts per candle respectively expressed as functions of the pressure in volts kept constantly on the lamp, and if p were the price of a lamp and H the price of one watt-hour, then the cost per hour per candle equalled

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[*] Communicated by the Physical Society: read December 14, 1894, and January 25, 1895.

[†] Phil. Mag. April 1885, p. 305.

$$\frac{p}{\mathrm{L}(v) \times \mathrm{C}(v)} + \mathrm{H} \times \mathrm{W}(v),$$

and the value of v which made this expression a minimum, they showed, was the proper P.D. to employ with the particular type of lamp.

The authors gave two methods of solving this problem defined by their equation of cost—the one a graphical method, and the other an analytical one. The graphical method consisted in drawing curves from the best experimental results then available to represent L(v), C(v), and W(v) respectively in terms of v, and from these three curves finding the values of L(v), C(v), and W(v) for many values of v, then, by substitution in the cost equation, data were obtained from which a last curve showing the relation between potential difference and cost per hour per candle could be drawn.

The curves on p. 45, Proc. Phys. Soc. vol. vii. 1885*, showed the results obtained when this method was applied to the case of 16 C.P. 100-volt Edison lamps, using as experimental data the results of tests, made at the Finsbury Technical College, on the relations between candles, volts, and watts, and the values of the life of this type of lamp when run at different pressures, as published by M. Foussat.

The curve AAA showed the cost per candle for lamp renewals during 560 hours when the price of a new lamp was five shillings; BBB the cost per candle for power during the same period, one horse-power for 560 hours being reckoned at £5, and CCC gave the total cost per candle for 560 hours. The ordinate of this latter curve had a minimum at about 101·4 volts.

With the analytical method, on the other hand, empirical equations were first found to represent as nearly as possible the experimental results. Thus it was found that

$$\frac{1}{\mathrm{L}(v) + \mathrm{C}(v)} = 10^{0\cdot07545\,v - 11\cdot697}$$

and

$$\mathrm{W}(v) = 3\cdot7 + 10^{8\cdot007 - 0\cdot07667\,v};$$

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* Phil. Mag. *tom. cit.* p. 308.

therefore the total cost per hour per candle equalled

$$p\,10^{0\cdot07545\,v-11\cdot697}+\mathrm{H}(3\cdot7+10^{8\cdot007-0\cdot07667\,v}).$$

From this equation, using the same values for the price of lamps and power as before, it was shown that to make the cost a minimum the P.D. maintained between the lamp-terminals should be 101·1; a result in close agreement with that obtained graphically.

At the next meeting of the Physical Society a paper was read by Dr. Fleming *, in which he considered what proportion the cost of lamp renewals should bear to the cost of power in order that the total cost should be a minimum. As the result of the examination of various experiments, he showed that for any particular type of lamp the average life could be expressed as an exponential function of either the watts per candle, or of the candle-power, or of the P.D.; that is, he showed, for the lamps with which he was dealing, that

$$\mathrm{L}=\frac{\mathrm{A}}{\mathrm{W}^{\alpha}}=\frac{\mathrm{B}}{\mathrm{C}^{\beta}}=\frac{1}{v^{\gamma}},$$

where L was the life, W the watts per candle, C the candle-power, v the P.D., and A, B, α, β, and γ constants for any particular type of lamp. Then, by substitution in the cost equation already referred to, he obtained the result that for maximum economy the cost of power must be to the cost of renewals as $\alpha\frac{\beta-1}{\beta}$ to unity. The values for α and β he gave for Edison lamps as $6\frac{1}{4}$ and $4\frac{1}{6}$ respectively; so that he finally arrived at the result that, whatever the price of lamps, or of electrical energy, the pressure used must be such that the annual cost of renewals should be about 17 per cent. of the total annual cost.

In April 1888, in a paper read before the American Institute of Electrical Engineers, Mr. Howell gave numerous examples of the application of Ayrton and Perry's graphical method to the finding of the efficiency at which various types of lamps should be run to obtain maximum economy for various prices of lamps and power.

He gave a curve showing the results of his tests of Edison lamps when run at different efficiencies, but the lamps he used were so abnormally good, compared with any with which we are acquainted, that his experiments have no practical value. For example, his lamps run at 4·5 watts a candle lasted, he says, nearly 12,000 hours.

Further, Mr. Howell's paper can hardly be said to have

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* Phil. Mag. May 1885, p. 368.

advanced the matter beyond the point at which it was left by the considerations contained in the paper on "The Most Economical Potential Difference, &c.," read before this Society in 1885; for he took no account of the changes which more recent experiments had shown to occur in lamps during their life, and which render any results obtained by methods that disregard these changes useless for practical purposes.

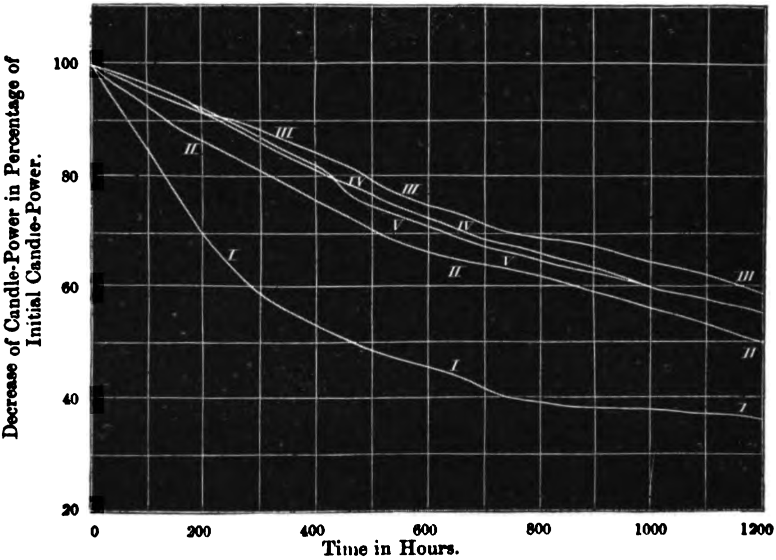
Numerous experimenters had found out that there was a serious diminution in the light emitted by a lamp as it grew old, and also a very considerable rise in the watts consumed per candle. Further, there was evidence to show that the shape of the curve between candle-power and time was not the same for different pressures; so that it had come to be recognized that, in order to determine the P.D. at which lamps should be run, it was useless to make a comparison merely between the efficiency of lamps when new and the number of hours they will last at various voltages.

Moreover, this falling-off in the quality of a lamp as it ages led people to consider another point, viz., Might it not be possible, in consequence of this deterioration, for a lamp to be economically dead before the filament had actually broken? For the increased cost of the current required, compared with the light given out, might more than overbalance the expense of replacing the lamp with a new and, therefore, more brilliant one.

Before describing the results which we have obtained regarding this interesting question of the existence of a point, called by the Americans the "smashing point," beyond which a lamp cannot be economically used, it will be well to shortly indicate the general conclusions to which previous experimenters have been led from tests on the modern glow-lamp.

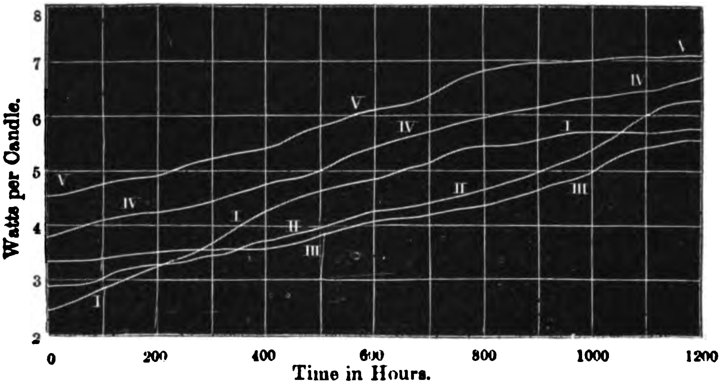
In November 1892 Mr. Feldman published a table compiled from the results of tests made by Prof. Thomas and Messrs. Martin and Hassler in America, by M. Haubtmann in France, and from some of his own measurements, which contained mean values for more than 500 lamps taken from 28 different factories and representing 49 different types. He divided the lamps into five groups according to their initial efficiencies, and gave for each group the average candle-power in per cent. of the initial candle-power and the average watts per candle at every hundred hours in the lives of the lamps. The curves in figs. 1 and 2 are drawn from the figures given in this table, fig. 1 showing the candle-power and fig. 2 the watts per candle as the lamps grow old. The numbers I., II., III., IV., and V. on the curves refer to the initial efficiencies

Fig. 1.—Tests of American and European Lamps.



Curves marked	Initial Watts per Candle.
I.	From 2·0 to 2·5
II.	From 2·5 to 3·0
III.	From 3·0 to 3·5
IV.	From 3·5 to 4·0
V.	Over 4.

Fig. 2.

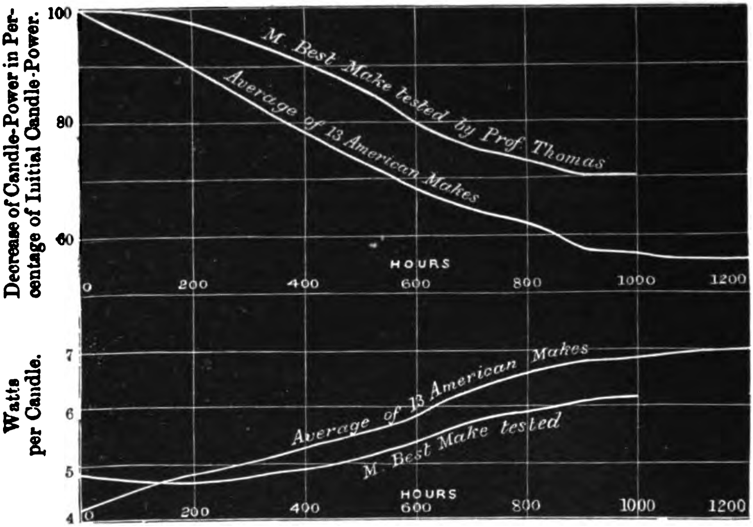


of the lamps whose behaviour the curves illustrate, and, as seen from the table on fig. 1, the curves marked I. are drawn from results obtained from lamps which initially required from 2 to 2·5 watts per candle; for curves marked II. the initial consumption was 2·5 to 3 watts per candle; for curves III. from 3 to 3·5; for curves IV. from 3·5 to 4; and for curves V. above 4 watts per candle.

These curves show that the fall in candle-power varied from 40 to 65 per cent. in 1200 hours, or, rejecting lamps having as low an initial consumption as from 2 to 2·5 watts per candle, Mr. Feldman's curves would lead us to expect that the candle-power of an average lamp would fall about 40 per cent. in 1000 hours.

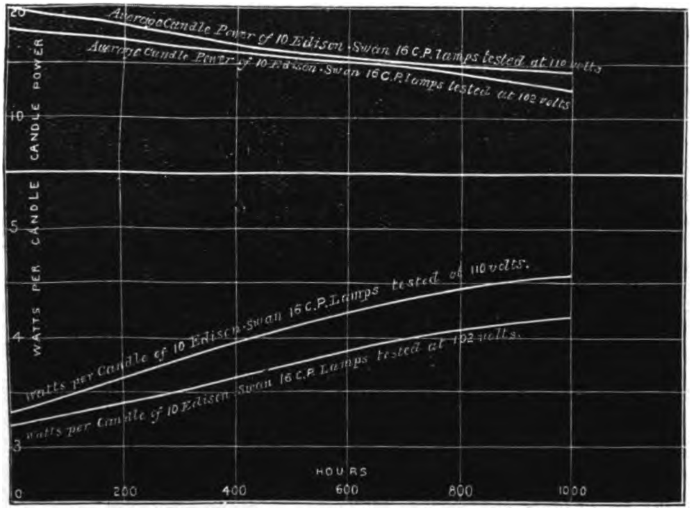
From the curves marked A in fig. 3, which give the results of Professor Thomas' tests made in 1892 on 127 lamps of 13 American makes, it can be seen that the average American lamp of that date dropped about 43 per cent. in candle-power in 1000 hours, the watts per candle in the same time rising from 4·2 to 6·9. The curves marked M on the same figure show the results obtained from the best make of lamp tested by Professor Thomas; the average of the 10 lamps tested showed a drop of 30 per cent. in candle-power in 1000 hours, and a rise from 4·8 to 6·1 in watts per candle.

Fig. 3.—Prof. Thomas' American Tests.



In September 1892 M. Haubtmann published tests on many European makes of lamps. The curves in fig. 4 show the results he obtained from testing twenty 16 C.P. Edison-Swan lamps, ten at 102 and ten at 110 volts. Those run at 102 volts showed a drop of about 30 per cent. in candle-power in 1000 hours, the watts per candle rising in the same time from 3·27 to 4·4; the lamps run at 110 volts in 1000 hours dropped 28 per cent. in candle-power and rose from 3·35 to 4·58 watts per candle.

Fig. 4.—Tests by M. Haubtmann on 20 similar 16 Candle-Power Edison-Swan Lamps, 10 of which were run at 110 volts and 10 at 102 volts.



If, now, in the light of the knowledge obtained from these experiments, we look at the equation of cost quoted in the beginning of this paper, we see that some changes must be made in it before it expresses the truth. As originally given it was:—Cost per hour per candle equals

$$\frac{p}{L(v) \times C(v)} + H \times W(v);$$

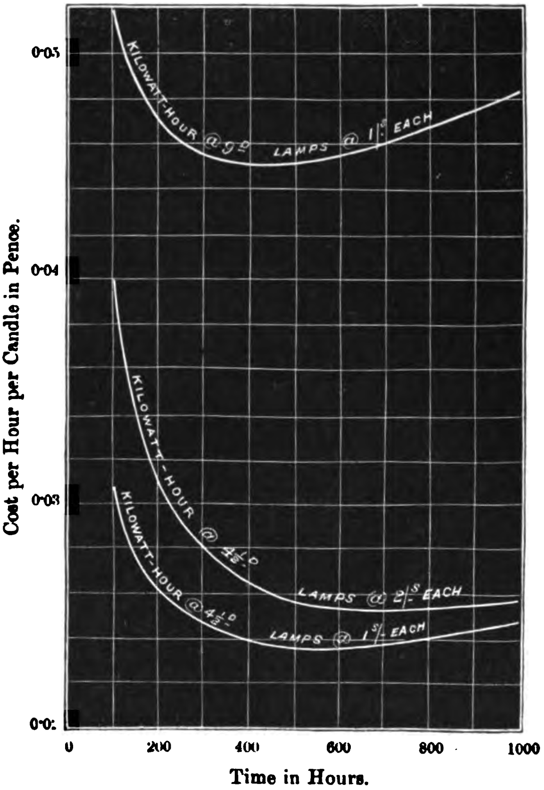
but, as neither the candle-power nor the watts per candle remain constant throughout the life of the lamp, $L(v) \times C(v)$ does not give the total candle-hours obtained during the lamp's life, and neither does $H \times W(v)$ give the true cost of power per hour per candle. The equation must, therefore, be written:—Cost per hour per candle equals

$$\frac{p}{\text{total candle-hours}} + H \times \textit{average} \text{ watts per candle.}$$

Exactly what these changes in the equation mean will be best shown by working out the results for a particular type of lamp, and for this purpose we have chosen the American make tested by Professor Thomas, the life curves of which are shown marked M in fig. 3.

It is clear, from these curves, that knowing the initial candle-power, in this case about 12·5, we can calculate at any time during the life of a lamp the total candle-hours obtained and the average watts consumed per candle during that time, and by substituting these quantities in the equation of cost we can find the cost per hour per candle averaged over the number of hours considered.

Fig. 5.—Cost Curves calculated for American make M in fig. 3.



The curves in fig. 5 show the results we have obtained when these calculations are made at different times in the life of a lamp, and for different prices of lamps, and of power.

In calculating the figures from which the bottom curve is plotted, we have taken the cost of a new lamp as one shilling, and the price of a Board of Trade unit as 4½*d.*, and, as seen, the ordinate of this curve reaches a minimum at about 600 hours, when the cost per hour per candle has dropped to 0·0235 pence. Beyond this point the curve begins to ascend; that is, when a new lamp costs one shilling, and a kilowatt-hour 4½*d.*, and lamps whose life-histories are truly represented by the curves M in fig. 3 are employed, the cost of obtaining light is least if the lamps are used for 600 hours only, because after that time their diminished quality more than overbalances the cost of renewing.

A change in the price of lamps does not much affect the economical life, as is shown on fig. 5 by the middle curve, which we have calculated for the same price of power but on the assumption that a new lamp costs two shillings. The ordinate of this curve has a minimum value at 650 hours instead of at 600 hours, when a new lamp was supposed to cost one shilling only.

The higher the price paid for energy the more important does this question of economical life become, and the sooner is it necessary to discard lamps, because the cost of renewals bears a less proportion to the total cost. This is illustrated in fig. 5 by the top curve, to obtain which we have assumed that the cost of energy was 9*d.* a unit, and the price of a new lamp one shilling. Now the minimum point falls to 430 hours instead of being at 600, at which it stood when the price of the Board of Trade unit was taken as 4½*d.*

When cost curves, like those in fig. 5, are drawn for a worse type of lamp, the minimum point becomes more sharply defined and is reached earlier. It might be urged, however, that all such curves merely indicate for how many hours lamps should be used in order that the price paid for the light may be a minimum, but that, if at the end of that time the light given out by the lamps is sufficient for the purpose for which they are intended, surely it would be folly to discard them. The answer to this is, that the lamps employed were of too high candle-power for the necessary illumination, and what should be done is to throw away the nominally higher candle-power lamps that have deteriorated and replace them with new *lower* candle-power lamps.

When, therefore, the special investigation which forms the subject of this paper was commenced at the end of 1892, there was good reason for expecting, first, that with any type of glow-lamp a certain number of hours could be experimentally determined at the end of which it would be economical to discard lamps even when the price of a Board of Trade unit was as low as 4½*d.*; secondly, that it was only economical to run lamps at the pressure marked on them for one particular price of electric energy.

As Edison-Swan lamps were the only lamps that could be legally used in this country in 1892, and as a pressure of 100 volts was one very commonly employed for electric lighting, we decided to experimentally find out what was the most economical pressure to maintain between the terminals of nominal 100-volt 8-candle lamps of this make, and what was the length of their economic lives for different prices of a Board of Trade unit.

As it is well known that the lives of filaments are considerably affected by the steadiness of the pressure between their terminals, it was decided to run the lamps from a battery of storage-cells, and to arrange that the pressure when on the lamps should not vary by as much as one tenth per cent. The capacity, however, of the cells at the Central Technical College which could be entirely set on one side for this investigation and used for running 100-volt lamps from five o'clock every evening to nine or ten o'clock the next morning for five nights of the week, only allowed of nine 8 C.P. lamps being dealt with at a time. The nine lamps were divided into three groups, each containing three lamps, and a perfectly constant, but different P.D. was maintained between the terminals of the lamps in each group.

When our experiments were begun it was known that the price of lamps would fall in the autumn of 1893, therefore it was considered hardly probable that any economy would be gained by running the lamps at less than their normal pressure. Hence we decided to run the three groups at 100, 102, and 104 volts respectively. The tests, however, soon proved that no economy could be gained by running these lamps at as high a pressure as that of 104 volts, and so the group running at that pressure was changed for one running at 101 volts.

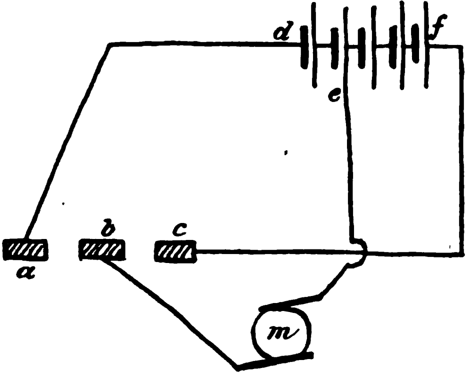
The pressure of the storage-cells which supplied the lamps with current diminished, of course, during the night, so that it was necessary to introduce between the cells and the lamps a variable resistance which could be altered to keep the pressure on the lamps constant within one tenth per cent., and to avoid constant attention it was also necessary that this resistance should be automatically controlled.

As no automatic regulator could be purchased which would keep the pressure throughout the night within one tenth per cent. of the desired value, it was necessary to construct such an instrument.

The apparatus which we employed for this purpose resembled generally the one described in a paper on "The Working Efficiency of Secondary Cells" by Messrs. C. G. Lamb, E. W. Smith, M. W. Woods, and one of the authors of the present communication, *see* Journ. Inst. Elect. Eng. vol. xix. 1890.

A variable resistance, consisting of four platinoid wires winding on and off a brass roller, was placed in the main circuit between the cells and the lamps. This resistance was geared to a permanent magnet Gramme-motor, the electrical connexions of which are shown in fig. 6. *d e f* was a battery of five storage-cells to the centre *e* of which one brush of the motor *m* was connected, the other brush being joined to the middle cup *b* of a three-way mercury switch *a b c*. The two outer cups *a* and *c* of this switch were connected with the two ends *d* and *f* of the battery.

Fig. 6.



It is clear from the figure that the motor revolved one way or the other according as *a* and *b* or *b* and *c* were connected.

A "set up" d'Arsonval galvanometer in series with a resistance was placed across the two points in the main circuit between which it was desired that the pressure should remain constant. To the coil of this galvanometer was attached a pointer ending in a platinum tip which worked between two platinum contacts. The phosphor-bronze strip by which the coil of the d'Arsonval was suspended was twisted several times, so that when the pressure on the lamps was correct the tip of the pointer rested midway between the contacts. If, however, the pressure rose by one tenth of a volt the pointer was deflected and made to touch one of the contacts, and so to complete the circuit of an electromagnet: this, by closing one side of the mercury switch (fig. 6), started the motor, which increased the resistance in the main circuit until the pressure was correct again.

Exactly the opposite happened if the pressure fell, the pointer touched the other contact, the other side of the mercury switch was closed, and the motor working in the reverse direction reduced the resistance between the cells and the lamps.

The pointer was kept from sticking to its contacts by a light wooden hammer which tapped the case of the galvanometer when the motor revolved.

By means of this apparatus it was possible to keep the pressure constant to within at least one tenth per cent.

For many nights the action of this regulator was watched pending the arrival of a recording voltmeter, but the recording voltmeter not being forthcoming, and staying up all night, even for four times a week, interfering much with our work during the day, we decided to construct an automatic check on the automatic regulator.

In series with the first galvanometer was placed a second working in exactly the same way, but with its contacts so far apart that its pointer only touched them for a rise or fall of half a volt in the pressure on the lamps. When for any reason such an alteration took place, the pointer of this second galvanometer, by touching one of its contacts, completed the circuit of an electromagnet; this attracted a piece of soft iron which opened a mercury switch and put out the lamps, and at the same time by stopping a clock indicated the time at which the irregularity took place.

Besides acting as a check on the regulating apparatus, this automatic cut-out worked whenever the pressure rose on a lamp breaking, and so made it possible to tell the exact life of the broken filament.

The lamps being tested were arranged in the special stand shown in fig. 7. The circular plate A, which could be turned on the centre pillar B, was divided into six compartments by the radial divisions shown, and the nine lamps simultaneously tested were placed in three of these compartments, which were coloured a dead black inside. The whole was covered up with an outer tin case, drawn in broken lines, which was fixed to the uprights C, D, E, F, and had an opening in front through which any one of the groups of lamps could be seen when turned into position.

When photometric measurements were not being made, the top of the case was left open to let out the heat.

The arrangements for measuring the current and for bringing it to the lamps are sketched in fig. 8. M and N

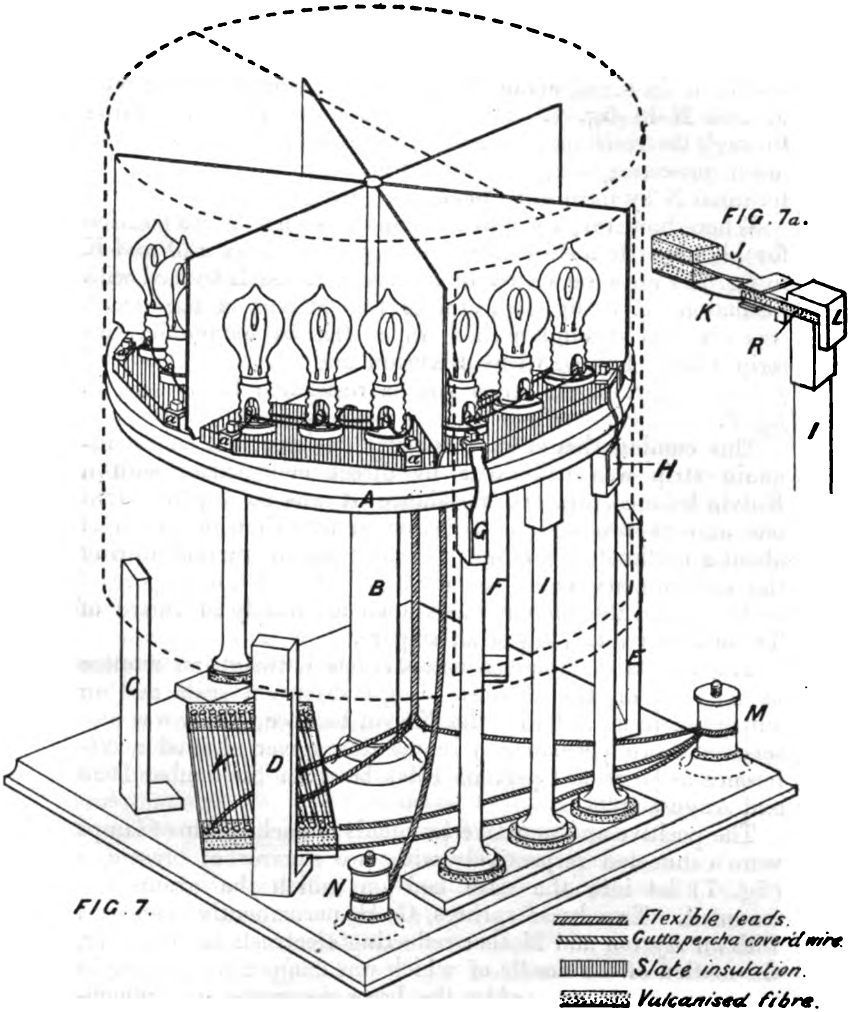
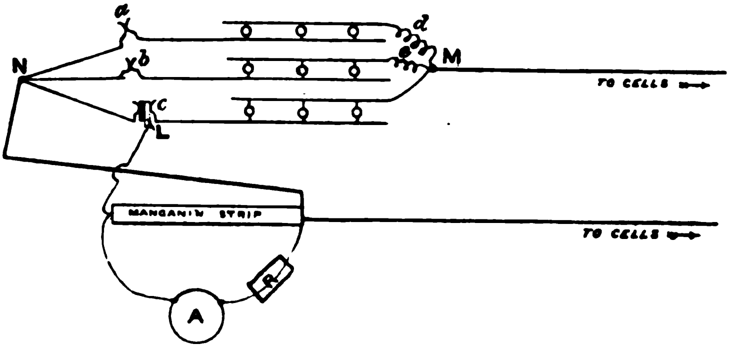


FIG. 7a.
J
K
L
R
I
A
B
C
D
E
F
G
H
I
K
M
N
a
FIG. 7.
Flexible leads.
Gutta percha coverd wire.
Slate insulation.
Vulcanised fibre.

Fig. 8.


a
b
c
d
e
N
M
L
TO CELLS
MANGANIN STRIP
TO CELLS
A
R

are the main terminals of the lamp-stand, corresponding with M and N in fig. 7. From M the current, after passing through the resistances *e* and *d*, for the two groups run at lower pressures, went through the lamps and reached the terminal N by means of the copper springs *a*, *b*, and *c*.

When, however, a group of lamps was turned into position for photometric measurements its copper springs *c* (J and K in fig. 7*a*) were separated by a piece of brass L backed with insulation (R in fig. 7*a*), and so the current of the group was diverted through a thick wide strip of manganin, this strip being shunted with an Ayrton and Mather d'Arsonval galvanometer, A, in series with a resistance R, as seen in fig. 8.

This combination of galvanometer, resistance R, and manganin strip was calibrated by direct comparison with a Kelvin balance, and the resistance R was so adjusted that one ampere produced a deflexion of 500 divisions, each of about a millimetre in length. Variations of current during the experiments could be read to $\frac{1}{5000}$ of an ampere if required, and the current was known accurately in Board of Trade amperes to $\frac{1}{1000}$ of an ampere.

The results of frequent comparisons between an ampere as read off on the direct-reading transparent scale and an ampere as measured with the Kelvin balance, which was also screwed down permanently in position, never showed a difference as large as 1 part in 1500 between September 1893 and August 1894.

The positive and negative terminals of each group of lamps were connected respectively with two squares of brass *a*, *a* (fig. 7) let into the slate bed on which the group was mounted. Two brass springs, G, H, permanently connected with an Ayrton and Mather reflecting electrostatic voltmeter, the motion of the needle of which was damped by moving in a magnetic field, pressed on the brass squares *a*, *a* of whichever group of lamps was brought to the front of the stand.

The zero of the voltmeter was so arranged that the transparent scale, which was direct-reading, was nearly uniformly divided from 50 to 120 volts, each division of about 1·5 millimetre representing 0·2 volt, so that it was easy to read the deflexion to within 2 parts in 10,000.

The electrostatic voltmeter was frequently calibrated, and the maximum change in sensibility between July 1893 and August 1894 did not exceed 0·2 per cent. This change, although small, is fully accounted for by the variation in the zero, since the instrument did not possess the delicate zero adjustment of the later specimens of this type of voltmeter.

The standard of light we used was a two candle-power Methven screen fed with *pentaned* gas, and against this a ten candle-power Bernstein glow-lamp was standardized to give five candles, the Bernstein lamp being employed for the actual comparison with the Edison-Swan lamps.

One of the objects of employing this Bernstein lamp was to test whether or no a convenient and trustworthy standard of light could be obtained by using a low-voltage lamp with its filament at a comparatively low temperature. From this point of view, however, the results were not very satisfactory, as at the end of some sixty hours of life the lamp had blackened heavily. This secondary standard was of course tested very frequently—as a rule, every time it was used.

For the last few hundred hours of our tests an 8 C.P. 100-volt Edison-Swan lamp running at five candles was used as an intermediate standard of light, and after the first few hours it gave very fair results, the current required to produce exactly five candles dropping in almost a straight line from 0·3893 to 0·3867 ampere in two hundred hours. It is probable, for reasons which will be shortly apparent, that an even better result would have been obtained if the lamp had been run for some fifty hours at its normal brilliancy before it was used as a standard of light.

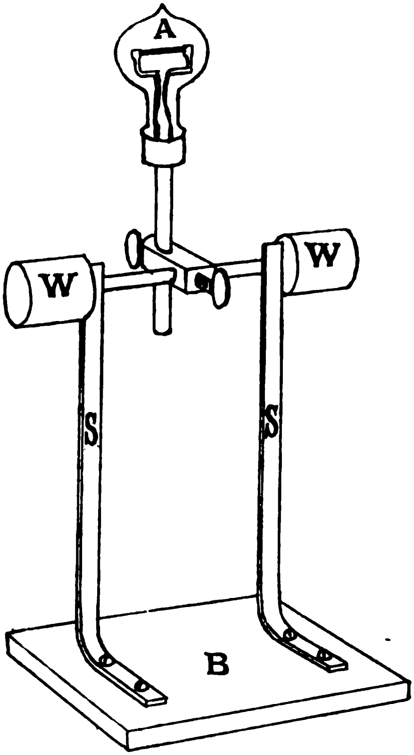
For measuring the light a Lummer-Brodham photometer was used, and proved itself a very convenient instrument. The lamp-stand was fixed at the end of a three-metre photometer bench, the actual distance between the standard and the Edison-Swan lamps being 319·5 centims.

Some difficulty was found at first in measuring the candle-power owing to the very considerable difference in colour between the lights being compared. This difficulty was considerably reduced by fixing the Bernstein lamp to the spring frame shown in fig. 9, where A is the lamp, S, S are steel springs, and W, W are leaden weights.

When measurements of the candle-power were being taken, the Bernstein lamp was set gently swinging backwards and forwards in the direction of the bench, and the effect thus easily produced was found to be an improvement on that usually obtained by moving the photometer first a little on one side, and then a little on the other, of the neutral point. After some practice the use of this contrivance enabled us to make measurements of the candle-power which did not differ from each other by more than 0·3 per cent.

The first point noticed after starting the tests was that candle-power, current, and candles per watt all *rose* as the lives of the lamps increased; and as we were not prepared, from the published accounts of experiments previously made on glow-lamps, to expect any such result, we thought it

Fig. 9.



might be due to some error in our measurements. We therefore made a number of tests to satisfy ourselves that this was not the case.

A current nearly twice as large as the maximum required to be measured was sent through the manganin strip for several hours, but the deflexion of the d'Arsonval galvanometer for a given current was not altered, so that the effect was certainly not due to the heating of the strip or galvanometer-coil.

As the voltmeter was connected with the terminals of the lamp sockets and not with the terminals of the lamps themselves, we tested whether any resistance was introduced by the sockets, or whether any alteration occurred when they got warm after the lamps had been glowing for some hours.

An old lamp was taken and wires soldered to its terminals, and also to the terminals of the socket into which it was screwed, and, by measuring as nearly simultaneously as possible the pressures on the lamp and on the socket terminals under various conditions as to heat and position of lamp, we proved that the resistance of the socket and contacts was never perceptible.

There seemed, therefore, no reason to doubt the results already obtained; but as the accuracy with which the candle-power could be measured had increased with practice and with the introduction of the swinging frame, we decided after 110 hours of testing to start again with new lamps.

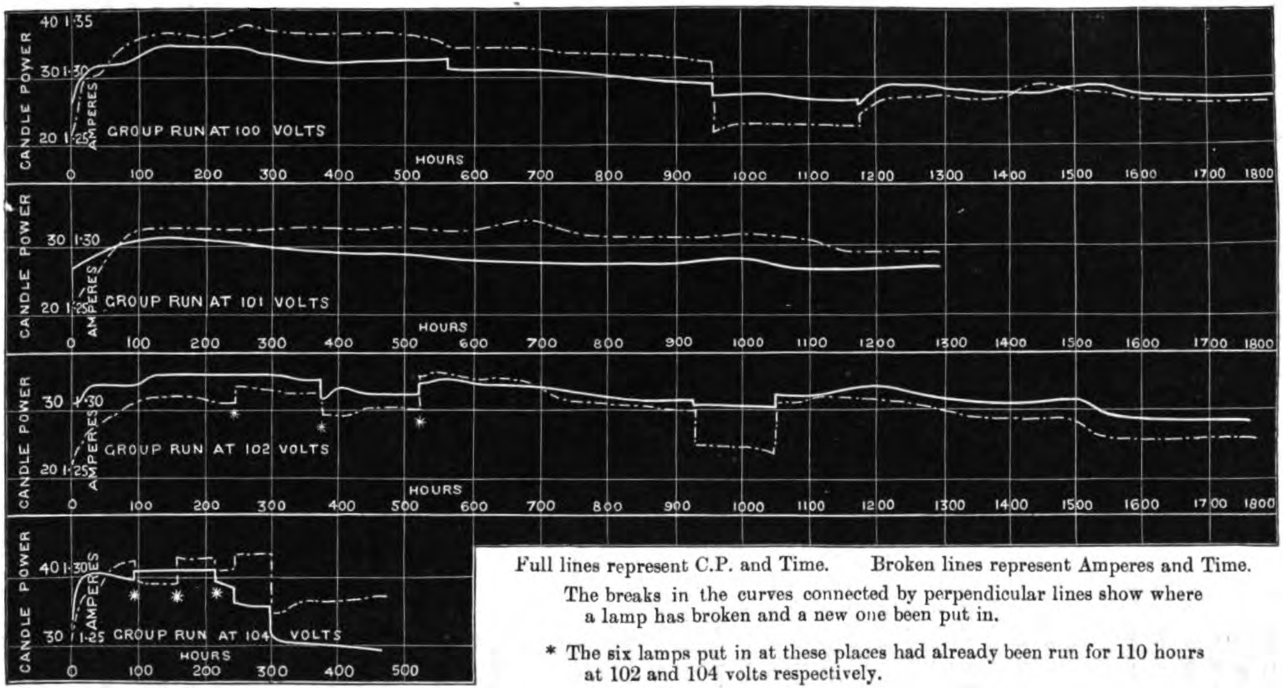
The results obtained in these preliminary tests are shown in fig. 10*a*, the curves in fig. 10 being those obtained from the lamps subsequently tested.

These curves show the variation of light and current with time for four groups of lamps between the terminals of which perfectly constant P.Ds. of 100, 101, 102, and 104 volts were maintained respectively, the full lines representing candle-power and the dotted lines current. The breaks in the curves connected by vertical lines indicate the times at which a lamp broke and was replaced by a new one, so that each group always consisted of three lamps.

All these curves show that the light given out by these Edison-Swan lamps was *greater* after they had been glowing for some time than it was when the lamps were new; also that even just before the filament of one lamp in a group broke, the total light given out by the group of three was greater than when the lamps were new. This is a totally different result from that obtained in earlier tests, as illustrated in figs. 1, 2, 3, and 4, which showed that a considerable deterioration in candle-power always took place after lamps had been running for some time. Further, while the globes of earlier lamps were always much blackened, even after a run of a few hundred hours, and so became comparatively useless long before the filament broke, the Edison-Swan lamps which we have been testing showed hardly any blackening, even when the filaments lasted for over 1300 hours.

The highness of the average candle-power of Edison-Swan lamps marked 100–8 after they have been run for some time at 100 volts, is corroborated by the figures in the following table, which gives the results of the measurements of the candle-power and the watts per candle of eleven 8-candle 100-volt lamps which had been run from the mains of the Notting-Hill Electric Lighting Co. As these lamps had been used in different rooms of a dwelling-house, it was

Fig. 10.—Life Tests on Edison-Swan 8 C.P. 100-volt Lamps run at Various Voltages.

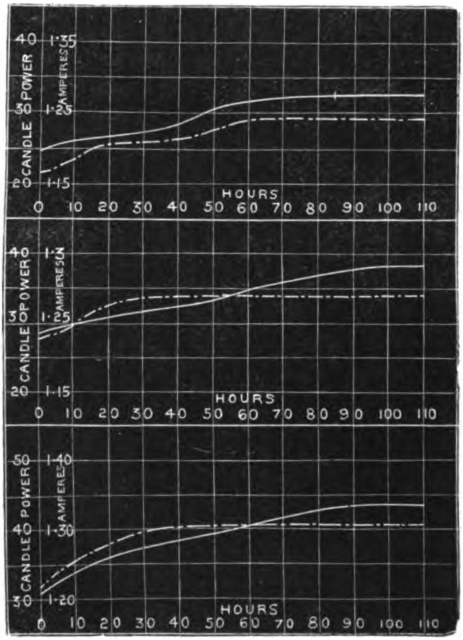


Full lines represent C.P. and Time. Broken lines represent Amperes and Time.

The breaks in the curves connected by perpendicular lines show where a lamp has broken and a new one been put in.

* The six lamps put in at these places had already been run for 110 hours at 102 and 104 volts respectively.

Fig. 10 *a*.—Preliminary Tests on Edison-Swan 8 C.P. 100-volt Lamps run at Various Voltages.



Group of 3 Lamps marked 100–8 run at 100 volts.

Group of 3 Lamps marked 100–8 run at 102 volts.

Group of 3 Lamps marked 100–8 run at 104 volts.

Full lines represent Candle-Power and Time.
Broken lines represent Amperes and Time.

impossible to say for how many hours they had been run, but the time probably varied from about 200 to 600 hours, and at any rate none of them were new.

The measurements were taken at 100 volts, and Harcourt's pentane burner was the standard of light used.

Candle-Power.	Watts per Candle.	Candle-Power.	Watts per Candle.
10·5	4·10	10·5	4·04
11·9	3·77	8·4	4·10
7·37	5·41	9·73	4·23
7·65	4·51	10·05	4·19
12·68	3·43	9·78	4·31
11·25	3·92		

In these lamps, as in the others we tested, the blackening of the bulbs was very slight indeed. Since the above measurements were made, the two lamps whose candle-powers were 11·9 and 11·25 have broken after about another hundred hours of life without, as far as could be judged, any diminution in their light or any increase in the blackening of their bulbs.

Moreover, although the rise of candle-power seen in figs. 10 and 10 *a* was always accompanied with a rise in current, yet, as the rise in candle-power was proportionally much greater than the rise in current for the lamps we tested, as will be seen from figs. 10 and 10 *a*, where one division represents 50 per cent. change in the light, but only 4 per cent. change in the current, the consumption of power per candle was actually *less* after the lamp had run for 50 hours than it was at the beginning, and the power per candle did not rise seriously during the whole life of a lamp.

Examining the results for the group run at 100 volts, we see that in the first 124 hours the candle-power rose from 26·3 to 35, or by 33·1 per cent., the current in the same time rising from 1·261 to 1·335 amperes, or by 5·87 per cent., so that during those first hours the watts per candle dropped from 4·79 to 3·82.

During the 1820 hours of running, three lamps broke in this group, their lives being 572, 957, and 1167 hours; the three still unbroken at the end of the tests had been run for 1248, 863, and 653 hours respectively.

Over the first 500 hours the average consumption of energy with the lamps run at 100 volts was at the rate of 4·0 watts per candle, over the second 500 hours 4·36 watts per candle, over the third 500 hours 4·55 watts per candle, and over the whole run the average efficiency was 0·23 candle per watt, corresponding with 4·35 watts per candle.

The candle-power of the three lamps run at 101 volts rose in the first 150 hours from 26·5 to 30·6, that is by 15·5 per cent., the current rose from 1·27 to 1·33, or by 4·72 per cent., the watts per candle in the same time falling from 4·80 to 4·32. The average watts per candle over the whole run of 1340 hours of this group were 4·68, corresponding with an efficiency of 0·215 candle per watt.

In the group at 102 volts which was run for 1820 hours six lamps broke, their lives being 242, 372, 516, 570, 516, and 786 hours respectively in the order of breaking; the three lamps unbroken at the end of the tests had run for 1148, 898, and 772 hours respectively.

The initial rise in candle-power in this group at 102 volts was from 30·6 to 35, or a rise in 120 hours of 14·4 per cent., the current in the same time rose from 1·26 to 1·31 amperes, or by 3·97 per cent., so that the watts per candle diminished from 4·22 to 3·82.

The average consumption of energy during the first 500 hours was at the rate of 3·9 watts per candle, during the second 500 hours 4·06 watts per candle, during the third 500 hours 4·2 watts per candle, and over the whole run the average was 4·12 watts per candle, corresponding with an efficiency of 0·243 candle per watt.

Turning to the group run at 104 volts, the curves show that the breakages were very frequent. Altogether five lamps broke, their lives being 94, 175, 210, 242, and 254 hours; the three lamps left unbroken at the end of the test had been run for 165, 222, and 364 hours.

The initial rise in candle-power was from 33·8 to 40·5 candles, that is 19·8 per cent.; and the current rose from 1·264 to 1·307 amperes, or by 3·4 per cent.

Over the whole run the average watts per candle, for the lamps run at 104 volts, were 3·6, corresponding with an efficiency of 0·278 candle per watt.

It is known from preceding tests (see the 'Electrician,' July 15th, 1892, for example) that the light given out by a new glow-lamp varies approximately as the seventh power of the pressure when the pressure is something like the normal pressure for the lamp. Now, as the groups of lamps that we tested at 100, 102, and 104 volts respectively were selected so that each group gave practically the same light initially when tested at the same pressure of 100 volts, it was to be expected that the three groups run at the three different pressures would follow the law for the light given out by the same lamp when used at different pressures.

And this is practically the case, for if L_{100}, L_{102}, and L_{104} be the number of candles emitted by the three groups of three lamps each, we see from the curves on fig. 10 that at the start

$$L_{100}=26·3,\ L_{102}=30·6,\ L_{104}=32·5\ ;$$

$$\therefore\ \frac{L_{102}}{L_{100}}=1·16, \text{ and } \frac{L_{104}}{L_{100}}=1·24.$$

Hence the light is roughly as the seventh power of the pressure at the start.

But after the lamps have been glowing for 100 hours this relationship no longer holds, for after 100 hours from the start we see from the curves on fig. 10 that

$$L_{100}=33·9,\ L_{102}=34·1,\ L_{104}=39·8,$$

or

$$\frac{L_{102}}{L_{100}}=1,\quad \frac{L_{104}}{L_{100}}=1·17,$$

so that the light varies only as something like the fourth power of the pressure.

On the other hand, if we consider the results of the preliminary tests recorded in fig. 10*a*, we have at the start

$$L_{100}=24{\cdot}8,\quad L_{102}=28{\cdot}7,\quad L_{104}=30,$$

so that

$$\frac{L_{102}}{L_{100}}=1{\cdot}16,\quad \frac{L_{104}}{L_{100}}=1{\cdot}21\,;$$

while after 100 hours' run

$$L_{100}=33{\cdot}1,\quad L_{102}=38,\quad L_{104}=43{\cdot}3\,;$$

so that

$$\frac{L_{102}}{L_{100}}=1{\cdot}15,\quad \frac{L_{104}}{L_{100}}=1{\cdot}31.$$

In this case, then, the law of the seventh power holds roughly not only for the light given out by the three groups at the start but also at the end of the first 100 hours' run.

The following table gives the analysis of the chief results shown by the curves on figs. 10 and 10 *a*.

	Preliminary Tests.			Later Tests.			
Pressure in Volts maintained between Lamp Terminals	100	102	104	100	101	102	104
Duration of Test, in Hours	110	110	110	1,820	1,340	1,820	460
Initial Candle Power per Lamp	8·23	9·57	10	8·77	8·83	10·2	11·27
Initial Watts per Candle...	4·72	4·37	4·20	4·79	4·80	4·22	3·89
Largest Candle-Power per Lamp	11·1	12·6	14·5	11·67	10·23	11·67	13·5
Percentage Rise in Candle-Power at the beginning	35·0	31·9	45·0	33·1	15·5	14·4	19·8
Percentage Rise in Current at the beginning	7·55	4·87	7·43	5·87	4·28	3·97	3·4
Smallest Watts per Candle	3·74	3·48	3·12	3·82	4·3	3·82	3·33
Average Candle-Power per Lamp during whole run	...	...	...	10·0	9·4	10·7	12·1
Average Watts per Candle during whole run	...	...	...	4·35	4·68	4·12	3·6
Lives in Hours of Lamps Broken during run	...	...	...	572; 957; 1167.	No Lamps broken.	242; 372; 516; 540; 516; 786.	94; 175; 210; 242; 254.
Lives in Hours of Unbroken Lamps	...	...	...	1248; 863; 653.	1340; 1340; 1340.	1148; 898; 772.	165; 222; 364
Number of Lamps included in Striking Averages	...	...	...	6	3	9	8

Although, as already stated, the number of lamps that could be supplied with power every night at the Central Technical College was limited to nine, and although, therefore, the total number dealt with in the investigation was small, the curves on figs. 10 and 10*a*, and the results given in the preceding table, are quite sufficient to enable us to arrive at the following results :—

(1) When a group of Edison-Swan lamps marked 100–8 are run at 100 volts, and each lamp, as its filament breaks, is replaced by a *new* Edison-Swan 100–8 lamp, it may be expected that the light given out by the group will never be as small as it was at the beginning, when all the lamps in the group were new. This important result is brought about by the deterioration of the lamps with long-lived filaments being compensated by the great rise in the light given out by each new lamp when put in place of one whose filament has broken.

(2) An Edison-Swan lamp marked 100–8 when run at 100 volts will give an average illumination during its whole life of about 10 candles, and will absorb an average power of about 4·3 watts per candle, so that such a lamp must be regarded as a 43-watt lamp, and not a 30-watt lamp as is not unfrequently stated, this difference in power being about 43 per cent.

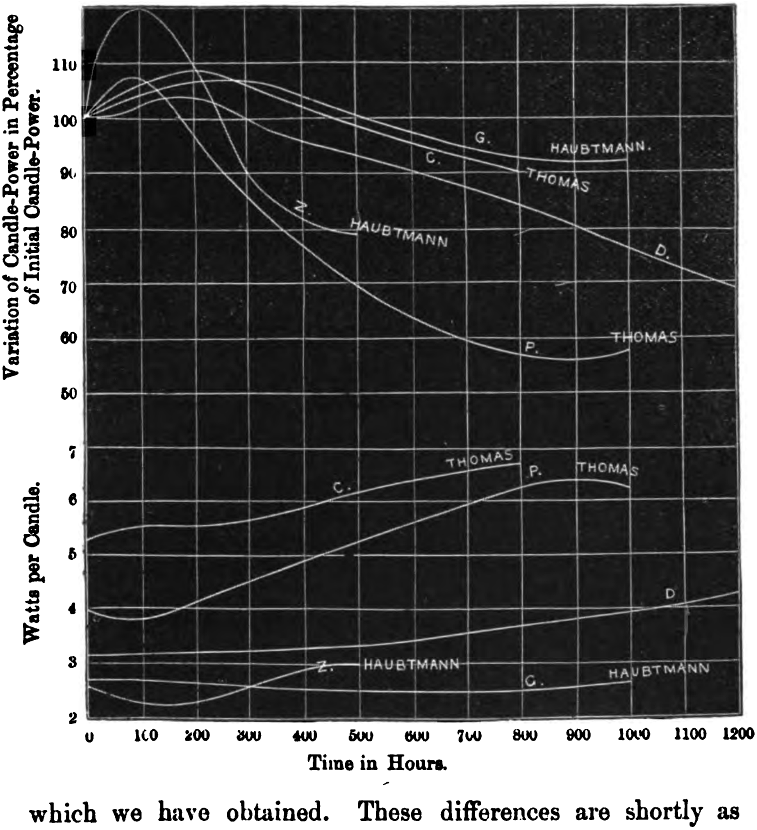
(3) An Edison-Swan lamp marked 100–8 may, when run at 100 volts, emit during a large portion of its life a light of as much as 11·7 candles, and absorb a power of about 44·6 watts, which is about 44 per cent. greater than the nominal 30 watts.

These last two facts are of great importance to dynamo-constructors, when specifying, as is frequently done, the number of lamps of a given type to which a given dynamo can supply current to without becoming too hot. For if, in making such a calculation, it be assumed that an Edison-Swan 8-candle-power lamp absorbs the nominal 30 watts, that is 3·75 watts a candle instead of the 44·6 watts which our tests show that such a lamp actually absorbs during a long portion of its life, the current will be 44 per cent. greater, and the rate of heating of the dynamo 108 per cent. greater, than was anticipated.

(4) Groups of new Edison-Swan lamps marked 100–8, if selected so as to give the same light at 100 volts, will, *when new*, emit a light which is roughly proportional to the seventh power of the pressure applied to them. But after a run of 100 hours, this rule connecting light and pressure may, or may not, hold.

The rise in candle-power with time, which occurred during the early part of the life of all the Edison-Swan lamps which we tested, may be noticed also in the collection of curves published by Mr. Feldman in the 'Electrician,' Nov. 29th, 1892 (fig. 11). But there are certain very important differences between the results recorded by these curves and those which we have obtained. These differences are shortly as follows:—

Fig. 11.



(1) The greatest rise of light emitted by the lamps as recorded in Mr. Feldman's curves was 14 per cent. In our experiments this maximum rise was 45 per cent.

(2) In spite of the first rise in the candle-power as shown in Mr. Feldman's curves (fig. 11), the candle-power at the end of the life of the lamps was in all cases much less than it was when the lamps were new. Whereas

with the lamps which we tested at 100, 101, and 102 volts the light given out by a group was never as low as it was at the beginning when the lamps were new.

(3) In spite of the first rise in candle-power recorded in the curves on fig. 11, it was only for the lamps whose behaviour was recorded in curves P and Z that the power expended per candle diminished at first with time. And even in the case of these two sets the power expended per candle increased again, and was greater when the filaments broke than it was when the lamps were new. Whereas in our tests the power expended per candle not only diminished considerably during the early life of the lamp, but it never rose again as high as it was when the lamps were new.

Although, then, the rise in candle-power during the early part of the life of a glow-lamp is apparently not an absolutely new fact, the magnitude of the rise and the effects resulting from it were, in the older lamps, so trifling that no special attention seems to have been devoted to this important subject in the former reports of tests of lamps. Indeed, even in a prominent book connected with glow-lamps which has quite recently been brought out in this country, no mention whatever is made of the fact in question. And yet, as we have already shown, and as will become more apparent from what follows, this remarkable rise in the candle-power during the earlier part of the life of an Edison-Swan lamp has a very important effect on the economy of lighting with glow-lamps.

The next point toconsider is the way in which the cost of lighting with the modern 100–8 Edison-Swan lamps depends on the pressure at which they are run, and on the cost of a Board of Trade unit. The curves on figs. 12 and 13 give the cost of obtaining light with the various groups of lamps, including the cost of replacing lamps with broken filaments, calculated day by day from our tests as the experiment went on.

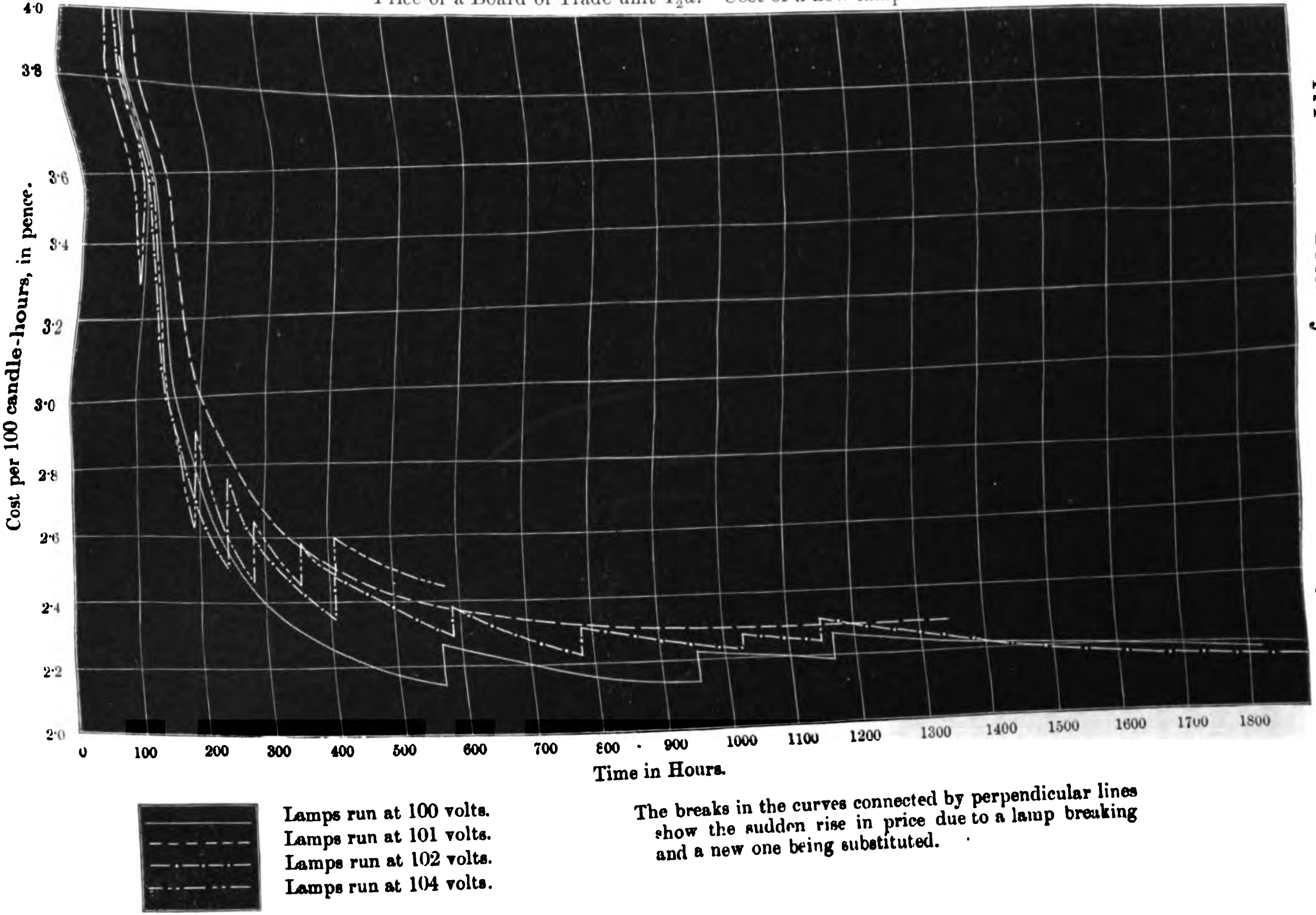
The ordinates of the curves show the cost of 100 candle-hours at any time during the test, time being measured horizontally, and the values of the ordinates have been calculated from the following formula:—

Total cost per candle per 100 hours at the end of any number of hours t equals

$$100 \times \frac{\text{Board of Trade units used during time } t \times \text{Price of one Board of Trade unit}}{\text{Total Candle-hours during time } t}$$

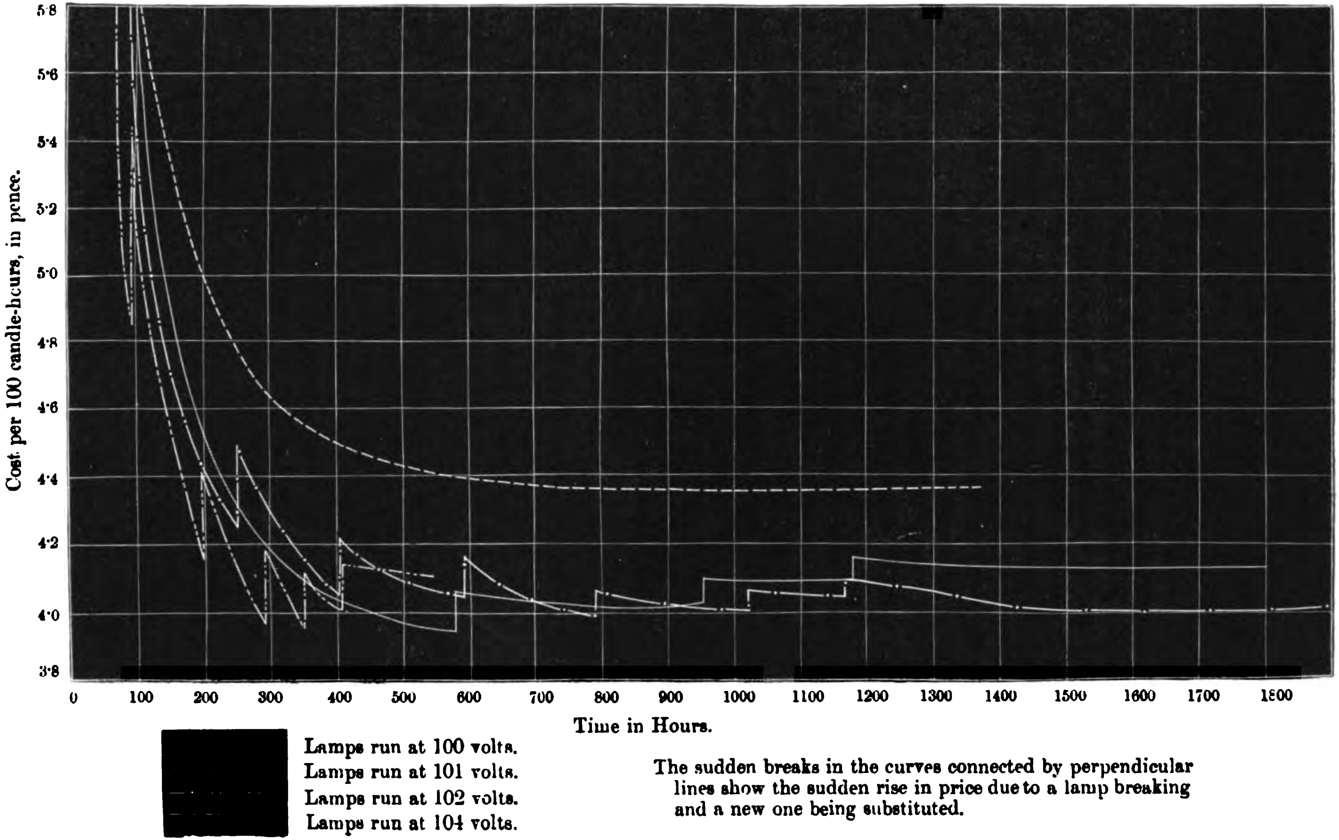
$$+ 100 \times \frac{\text{Number of lamps used during time } t \times \text{Price of one lamp}}{\text{Total Candle-hours during time } t}.$$

Price of a Board of Trade unit 4½*d*. Cost of a new lamp 1*s*. 9*d*.



The breaks in the curves connected by perpendicular lines show the sudden rise in price due to a lamp breaking and a new one being substituted.

Fig. 13.—Life Tests on Edison-Swan 8 C.P. 100-volt Lamps. Curves showing the relation between Cost of Light and Time. Price of a Board of Trade unit 9*d.* Cost of a new lamp 1*s.* 9*d.*



The sudden breaks in the curves connected by perpendicular lines show the sudden rise in price due to a lamp breaking and a new one being substituted.

The price of a kilowatt-hour we took as 4½*d* in fig. 12, and as 9*d*. in fig. 13, the cost of a new lamp being taken as 1*s*. 9*d*. in both sets of curves.

Of course, it will be seen from the formula quoted above, that whenever a lamp breaks and a new one is put in its place, there must be a sudden, though temporary, rise in the cost per candle-hour due to the cost of the new lamp; but this rise becomes less marked as the number of lamps included in the calculations increases, and would have become inappreciable if the tests could have been carried on for a sufficient length of time.

The first three lamps to break in both the 102 and the 104 volt groups were replaced by the lamps which we had previously run at 102 and 104 volts respectively for 110 hours; and in calculating the cost-curves we have added in the watt-hours and the candle-hours due to these previous runs; we have also added to the abscissæ of the curves the 110 hours.

On examining the total-cost curves on figs. 12 and 13, it is at once apparent that they nowhere show any such rise in the cost of producing light, as was seen in the similar curves for American lamps (fig. 5). The curves in fig. 12, for which the price of a Board-of-Trade unit was taken as 4½*d*., do *not* turn up *at any* point, not even for the three lamps run at 101 volts, which lasted unbroken for over 1300 hours.

In fig. 13, however, for drawing the curves on which the price of a Board-of-Trade unit has been taken at 9*d*., there are slight indications of the curves turning up: for example, the curve for the 100-volt group rises a little at 850 hours, at which time the lives of the three lamps being tested were 850, 850, and 278 hours; and, again, at about 1600 hours, when the lives of the three living lamps were 1028, 643, and 433 hours, the cost per candle-hour rises a little. In the group run at 101 volts the cost of lighting began to rise a little after the lamps had been lit for 1100 hours; and in the 102-volt group the curve (fig. 13) turns up a little at 1700 hours, at which time the ages of the lamps alight were 928, 678, and 552 hours. But at no one of these points is there a sufficient rise to indicate that a time has been reached when it would be good economy to discard lamps.

The remaining total cost curve on fig. 13, viz. that for the group of lamps run at 104 volts, when the price of the Board of Trade unit is taken at 9*d*., does not show any indication of a minimum point.

Hence, generally, we may conclude that when the modern Edison-Swan 8 C.P. 100-volt lamps such as we have been testing, costing 1*s*. 9*d*. per lamp, are supplied with energy costing 9*d.* per Board of Trade unit, no economy will be gained by discarding the lamps before the filaments break.

This important result is of course due to the fact, already pointed out, that there is no marked decrease in the candle-power of the lamps during their lives.

Owing to the extent to which the individual lamps varied among themselves, it is difficult to say which of the four pressures at which we tested lamps would be the most economical to use. The three lamps tested at 101 volts seem to have been quite abnormal, their efficiency being very low, and, as a consequence, their lives very long.

With a Board of Trade unit costing 4½*d.*, the lamps tested at 100 volts gave the cheapest light, and as they do not seem to have been above the average in quality this result may probably be safely taken as correct.

With energy costing 9*d.* per Board of Trade unit (fig. 13) there does not seem much to choose between the total cost of producing light with the three pressures of 100, 102, and 104 volts, excepting that the use of 104 volts would introduce an extra expense arising from the labour of frequently replacing broken lamps.

The two conclusions, then, to which we are led by a study of these total-cost curves on figs. 12 and 13 are :—

1. The modern Edison-Swan 8 C.P. 100-volt lamps such as we tested should not be discarded until the filaments break.
2. No marked economy can be gained by over-running this type of lamp.

Addition made January 25, 1895.

The question arises—what is the cause of the marked rise in candle-power which occurred with all the lamps tested by us during 1893 and 1894? In the early summer of 1894, when our tests were approaching completion, Mr. Howell, in contributing to a discussion at the American Institute of Electrical Engineers, stated that such a rise in candle-power was due to the vacuum of the lamp improving during the early part of its life. Therefore, after we had stopped the main investigation, we made some experiments to test the validity of Mr. Howell's explanation.

We applied the induction-coil vacuum-test to some dozen Edison-Swan lamps when quite new, and again after they had been run for about 80 hours at their normal pressure of 100 volts. In *every case* we found that the vacuum had apparently improved; for using a spark of about 8 millimetres in length, the lamps when *new* were entirely filled with a bright blue glow accompanied with some bright white patches on the glass; whereas, after a run of about 80 hours at a pressure of 100 volts, this phosphorescent effect with the 8 millimetre spark was either entirely absent, or consisted of only a faint nebulous glow which did *not* fill the lamp-bulb, and there was very little light on the surface of the glass.

Thus it appeared as if Mr. Howell's explanation of the great increase in the light given out by a glow-lamp during the early portion of its life was correct.

But this conclusion which we arrived at last year has been modified by tests that we have been carrying out on Edison-Swan glow-lamps purchased since our paper was sent in to the Physical Society in November 1894. For we find that,—while the induction-coil vacuum-test applied to these lamps when they are new, and after a run of 80 hours at the normal pressure of 100 volts, shows that the vacuum apparently improves,—this improvement in the vacuum is not accompanied with the great rise in candle-power which we found with all the Edison-Swan lamps purchased in 1892 and 1893, the tests of which form the subject of this paper. And yet the lamps are all marked in the same way, "100 E.F. 8," and they all look alike.

In the case of a set of these Edison-Swan lamps, purchased on January 21, 1895, not merely were the current and the light periodically measured, but the induction-coil vacuum-test was applied at intervals during the 80 hours' run; and it was found that the change in the phosphorescent appearance of the lamp, and the consequent apparent increase in the vacuum, was produced slowly and not suddenly on the first application of the pressure of 100 volts.

The following are the results of the tests of this batch of six lamps. The light was measured with a Harcourt-Pentane Standard, the potential difference with the Ayrton and Mather reflecting electrostatic voltmeter, and the current with the strip of manganin shunted with the Ayrton and Mather moving coil-galvanometer; this voltmeter and the ammeter combination being the same as those employed with all the lamps tested previously. But both instruments were carefully calibrated on January of this year, to make quite certain that the different behaviour of these newer lamps was not merely an apparent one produeed by some change having occurred in the sensibilities of the measuring-instruments.

The insulation of the lamp-holders was carefully cleaned and the contact-surfaces scraped before these tests were made.

Six Edison-Swan Lamps, marked "100 E.F. 8," purchased January 21, 1895, marked by us IX., X., XI., XII., XIII., XIV., and run at 100 Volts.

Filaments placed at an angle of 45° with the Photometer-Bench.

Hours of Running.	Power, in Watts.	Candle-Power.	Watts per Candle.
Lamp No. IX.			
0	41·3	9·70	4·26
1 hour 40 minutes.	41·3	9·70	4·26
6 hours 10 minutes.	41·5	9·70	4·28
13 hours 30 minutes.	41·6	9·67	4·30
42 hours 30 minutes.	41·9	9·85	4·25
80 hours	42·5	9·85	4·31
Lamp No. X.			
0	40·35	7·85	5·14
1 hour 45 minutes.	40·4	7·95	5·08
6 hours 15 minutes.	40·5	7·92	5·11
13 hours 35 minutes.	40·6	7·92	5·12
42 hours 35 minutes.	40·9	8·2	4·99
80 hours 5 minutes.	41·5	8·5	4·88
Lamp No. XI.			
0	39·8	7·89	5·05
1 hour 50 minutes.	39·8	8·00	4·97
6 hours 20 minutes.	39·8	8·11	4·91
13 hours 40 minutes.	39·8	7·95	5·01
42 hours 40 minutes.	39·8	8·00	4·97
80 hours 10 minutes.	40·1	8·00	5·01
Lamp No. XII.			
0	39·85	7·78	5·12
1 hour 55 minutes.	40·1	8·07	4·97
6 hours 25 minutes.	40·25	8·05	5·00
13 hours 45 minutes.	40·41	7·95	5·08
42 hours 45 minutes.	40·75	8·3	4·91
80 hours 15 minutes.	41·4	8·7	4·76
Lamp No. XIII.			
0	40·75	8·06	5·05
2 hours	40·6	8·06	5·04
6 hours 30 minutes.	40·5	8·17	4·95
13 hours 50 minutes.	40·5	7·85	5·15
42 hours 50 minutes.	40·5	7·9	5·13
80 hours 20 minutes.	40·6	8·4	4·67
Lamp No. XIV.			
0	41·2	8·49	4·85
2 hours 5 minutes.	41·2	8 65	4·76
6 hours 35 minutes.	41·2	8·65	4·76
13 hours 55 minutes.	41·2	8·49	4·85
42 hours 55 minutes.	41·2	8·6	4·80
80 hours 25 minutes.	41·5	8·5	4·89

From these tests it is seen that, in the case of lamps Nos. XI. and XIV., there was practically no change either in the light or in the power absorbed during the first 80 hours of. the running at the constant pressure of 100 volts; and that in the case of the remainder of this batch of lamps the increase in the light and in the power absorbed was comparatively small, the greatest change being with lamp No. XI., where the light rose by about 11 per cent. and the power by about 4 per cent. This is a very different result from that obtained with the Edison-Swan lamps previously tested, and run at a constant pressure of 100 volts, for there the total light given out by the three lamps together rose by 35 per cent. in the first 100 hours of running, and the power by 7·55 per cent.

Since, then, as already stated, the vacuum, when tested periodically with the induction-coil, appeared to improve steadily with each of the six lamps Nos. IX. to XIV. during the run of 80 hours, it would appear that improvement in the vacuum was *not* the sole cause, as stated by Mr. Howell, for the great rise in the candle-power such as we observed with all the Edison-Swan lamps which we tested in 1893 and 1894.

It is possible that this rise in candle-power may have been due to a change in the surface of the filament causing the emissivity for heat to decrease, since that would raise the light emitted, as well as the number of candles per watt. Whether such a change in the heat-emissivity of the filament occurs with time we have not yet found out.

Another point of difference between this batch of six lamps Nos. IX. to XIV. and those which we tested during the main part of our investigation, is the relative inefficiency of these six lamps. For in no single test at any time during the 80 hours run with these six lamps were the watts per candle less than 4·25, and in many cases they were over 5; while with lamp No. XIII. the watts per candle, as seen in the last table, were as high as 5·15 after this lamp had been run for 13 hours 50 minutes. It is possible, then, that when in the body of the paper we spoke of the group of three lamps which we ran at a constant pressure of 101 volts as being "quite abnormal," because the average watts per candle required with this group during the run of 1340 hours were as high as 4·68, we ought rather to have spoken of the various other groups of lamps which we ran at the constant pressures of 100, 102, and 104 volts respectively as being abnormally good Edison-Swan lamps.

At any rate it is clear that it is at present impossible to state the most economical potential difference to employ with any Edison-Swan lamps marked "100 E.F. 8;" since batches of lamps so marked, and therefore nominally the same, really require very different potential differences to be employed to obtain maximum economy with a given price of lamp and of a kilowatt-hour.

It may, however, be concluded, from the curves shown in figs. 12 and 13, that the most economical potential difference to employ with any Edison-Swan lamps marked "100 E.F. 8," such as have been obtainable in the open market since 1892, is the potential difference that will cause the lamp during a large portion of its life to have an efficiency of about 0·25 candle per watt, corresponding with 4 watts per candle.

The value of this potential difference for any batch of these lamps may be determined approximately in the following way. From our tests, already referred to, of eleven Edison-Swan lamps, marked "100 E.F. 8," which had been used in a house for some 200 or 300 hours, we found that the relation between candle-power and pressure was given by

$$\text{Candle-power} = a \times (\text{volts})^{5 \cdot 91},$$

where a is a constant. Also we found that the relation between candle-power and watts for these lamps was given by

$$\text{Candle-power} = b \times (\text{watts})^{2 \cdot 9},$$

where b is a constant. Therefore

$$\text{Volts} = c \times (\text{watts per candle})^{-0 \cdot 258},$$

where c is a constant.

Hence if one has a batch of Edison-Swan lamps marked "100 E.F. 8," whose efficiency is, say, 0·222 candle per watt, corresponding with 4·5 watts per candle, when a pressure of 100 volts is applied to them, it would be probably most economical to run them at about 103 volts, since this is the pressure which the last equation tells us will be necessary to raise the efficiency of such lamps to 0·25 candle per watt.

From what precedes, it follows that, since the average efficiency of the 100 E.F. 8 Edison-Swan appears to be less than 0·25 candle per watt, the opinion expressed by one of us in an article entitled "New Lamps for Old," published in the 'Electrician' for September 29, 1893, was correct, viz. that it would be economical to overrun Edison-Swan lamps by applying a pressure about 3 per cent. higher than the marked pressure. And that the reason why this conclusion was apparently negatived by the results of the tests which we carried out during the winter of 1893 and a large portion of 1894, was because the various groups of lamps which we ran at the constant pressures of 100, 102, and 104 volts respectively consisted of specially good specimens.

In applying the rule that the economical potential difference is about the one which causes the lamp to produce 0·25 candle per watt, it is important, however, to examine 8-candle 100-volt Edison-Swan lamps when bought to see whether they are really marked "100 E.F. 8." For while the result of various purchases of 8-candle 100-volt Edison-Swan lamps during the past three years has always resulted in lamps marked "100 E.F. 8" being sent us, although the marking on the lamps was never specified by us, a recent batch of lamps that we have received contained among them certain lamps marked "100 B. 8," which not only differed in the marking but also in the filament being of a simple horse-shoe shape, and not with a loop at the top as in the case of the other lamps. And, on testing these Edison-Swan B lamps, we were surprised to find that with no one of them, when run at 100 volts, did the watts per candle exceed 3·9, and in some cases the watts per candle were as low as 3·01. We have not, however, had these B lamps for a sufficiently long time in our possession to be able to express any opinion about their life-history.

XLI. *On the Change of Form of Long Waves advancing in a Rectangular Canal, and on a New Type of Long Stationary Waves. By* Dr. D. J. Korteweg, *Professor of Mathematics in the University of Amsterdam, and* Dr. G. de Vries[*].

INTRODUCTION.

IN such excellent treatises on hydrodynamics as those of Lamb and Basset, we find that even when friction is neglected long waves in a rectangular canal must necessarily change their form as they advance, becoming steeper in front and less steep behind[†]. Yet since the investigations of de Boussinesq[‡], Lord Rayleigh[§], and St. Venant[‖] on the solitary wave, there has been some cause to doubt the truth of this assertion. Indeed, if the reasons adduced were really decisive, it is difficult to see why the solitary wave should make an exception*; but even Lord Rayleigh and McCowan †, who have successfully and thoroughly treated the theory of this wave, do not directly contradict the statement in question. They are, as it seems to us, inclined to the opinion that the solitary wave is only stationary to a certain approximation.

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[*] Communicated by the Authors.

[†] It seems that this opinion was expressed for the first time by Airy, "Tides and Waves," *Encyc. Metrop.* 1845.

[‡] *Comptes Rendus*, 1871, vol. lxii.

[§] Phil. Mag. 1876, 5th series, vol. i. p. 257.

[‖] *Comptes Rendus*, 1885, vol. ci.

It is the desire to settle this question definitively which has led us into the somewhat tedious calculations which are to be found at the end of our paper. We believe, indeed, that from them the conclusion may be drawn, that in a frictionless liquid there may exist absolutely stationary waves and that the form of their surface and the motion of the liquid below it may be expressed by means of rapidly convergent series. But, in order that these lengthy calculations might not obscure other results, which were obtained in a less elaborate way, we have postponed them to the last part of our paper.

First, then, we investigate the deformation of a system of waves of arbitrary shape but moving in one direction only, *i. e.* we consider one of the two systems of waves, starting in opposite directions in consequence of any disturbance, after their complete separation from each other. By adding to the motion of the fluid a uniform motion with velocity equal and opposite to the velocity of propagation of the waves, we may reduce the surface of such a system to approximate, but not perfect, rest.

If, then, $l+\eta$ (η being a small quantity) represent the elevation of the surface above the bottom at a horizontal distance x from the origin of coordinates, we have succeeded in deducing the equation

$$\frac{\partial\eta}{\partial t}=\frac{3}{2}\sqrt{\frac{g}{l}}\cdot\frac{\partial\left(\frac{1}{2}\eta^2+\frac{2}{3}\alpha\eta+\frac{1}{3}\sigma\frac{\partial^2\eta}{\partial x^2}\right)}{\partial x},$$

where α is a small but arbitrary constant, which is in close connexion with the exact velocity of the uniform motion given to the liquid, and where $\sigma=\frac{1}{3}l^3-\frac{Tl}{\rho g}$ depends upon the depth l of the liquid, upon the capillary tension T at its surface, and upon its density ρ.

On assuming $\frac{\partial\eta}{\partial t}=0$ we of course obtain the differential equation for stationary waves, and it is easily shown that the well-known equation

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* Though the theory of the solitary wave is duly discussed in the treatise of Basset, the inconsistency of his result with the doctrine of the necessary change of form of long waves seems not to have sufficiently attracted the attention of the author.

† Phil. Mag. 1891, 5th series, vol. xxxii.

$$\eta = h\,\mathrm{sech}^2 x\sqrt{\frac{h}{4\sigma}}$$

of the solitary wave is included as a particular case in the general solution of this equation. But, in referring to this kind of wave, we have to notice the result that, taking capillarity into account, a *negative* wave will become the stationary one, when the depth of the liquid is small enough.

On proceeding then to the general solution, a new type of long stationary wave is detected, the shape of the surface being determined by the equation

$$\eta = h\,\mathrm{cn}^2 x\sqrt{\frac{h+k}{4\sigma}}\left(\text{mod. } \mathrm{M} = \sqrt{\frac{h}{h+k}}\right).$$

We propose to attach to this type of wave the name of *cnoidal* waves (in analogy with sinusoidal waves). For $k=0$ they become identical with the solitary wave. For large values of k they bear more and more resemblance to sinusoidal waves, though their general aspect differs in this respect, that their elevations are narrower than their hollows; at least when the liquid is not too shallow, in which latter case this peculiar feature is reversed by the influence of capillarity.

For very large values of k these cnoidal waves coincide with the train of oscillatory waves of unchanging shape discovered by Stokes*, which therefore *in the theory of long waves*† constitutes a particular case of the cnoidal form. Indeed the equation‡ obtained by Stokes, when written in our notation, becomes

$$\eta = h\cos\frac{2\pi x}{\lambda} - \frac{3h^2\lambda^2}{64\pi^2 l^3}\cos\frac{4\pi x}{\lambda};$$

but, as Sir G. Stokes remarks, in order that the method of approximation adopted by him may be legitimate, $\frac{\lambda^2 h}{l^3}$ must be a small fraction. Now, when capillarity is neglected, the wave-length λ of our cnoidal waves is equal to

$$\frac{4\mathrm{K}\sqrt{l^3}}{\sqrt{3(h+k)}},$$

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* Transactions of the Cambridge Phil. Soc. vol. viii. (1847), reprinted in Stokes, Math. and Phys. Papers, vol. i. p. 197.

† Stokes' solution is more general in so far as it applies also to those cases wherein the depth of the liquid is moderate or large in respect to the wave-length.

‡ Stokes, Math. and Phys. Papers, vol. i. p. 210.

and therefore

$$\frac{\lambda^2 h}{l^2} = \frac{16\mathrm{K}^2 h}{3(h+k)} = \frac{16}{3}\mathrm{M}^2\mathrm{K}^2.$$

This is a small fraction only when M, the modulus, is small, but the cnoidal waves then resemble sinusoidal waves; and it is obvious that in this case the equation of their surface may be developed in a rapidly convergent Fourier-series, of which Sir G. Stokes has given the first two terms.

After some more discussion about these cnoidal waves, concerning their velocity of propagation and the motion of the particles of fluid below their surface, we proceed to a closer examination of the deformation of long waves. To this effect we apply the equation for $\frac{\partial \eta}{\partial t}$ to various types of non-stationary waves, and it will appear that, though sinusoidal waves become steeper in front when advancing, other types of waves may behave otherwise.

I. *The Formula for* $\frac{d\eta}{dt}$.

In our investigations (in accordance with the method used by Lord Rayleigh, Phil. Mag. 1876, vol. i. p. 257, whose paper has been of great influence on our researches), we start from the supposition that the horizontal and vertical u and v of the fluid may be expressed by rapidly convergent series of the form

$$u = f + yf_1 + y^2 f_2 + \ldots$$
$$v = y\phi_1 + y^2\phi_2 + \ldots$$

where y represents the height of a particle above the bottom of the canal, and where $f, f_1, \ldots \phi_1, \phi_2, \ldots$ are functions of x and t. Of course the validity of this assumption must be proved later on by the fact that series of this description can be found satisfying all the conditions of the problem.

From one of these conditions, viz., the incompressibility of the liquid, which is expressed by $\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0$, we may deduce

$$\phi_n = -\frac{1}{n}\frac{\partial f_{n-1}}{\partial x},$$

and from another, viz., the absence of rotation in the fluid, expressed by $\frac{\partial u}{\partial y} - \frac{\partial v}{\partial x} = 0$:—

$$f_1 = 0\,;\ f_n = \frac{1}{n}\,\frac{\partial \phi_{n-1}}{\partial x} = -\frac{1}{n(n-1)}\,\frac{\partial^2 f_{n-2}}{\partial x^2}.$$

In this manner we obtain the following set of equations :—

$$u = f - \frac{1}{2}y^2\frac{\partial^2 f}{\partial x^2} + \frac{1}{24}\,y^4\,\frac{\partial^4 f}{\partial x^4} - \ldots \quad . \quad . \quad . \quad (1)$$

$$v = -y\frac{\partial f}{\partial x} + \frac{1}{6}y^3\frac{\partial^3 f}{\partial x^3} - \frac{1}{120}y^5\frac{\partial^5 f}{\partial x^5} + \ldots \quad . \quad (2)$$

and, moreover, if ϕ be the velocity potential and ψ the stream-function :—

$$\phi = \int f\partial x - \frac{1}{2}y^2\frac{\partial f}{\partial x} + \frac{1}{24}y^4\frac{\partial^3 f}{\partial x^3} - \ldots \quad . \quad . \quad . (3)$$

$$\psi = yf - \frac{1}{6}y^3\frac{\partial^2 f}{\partial x^2} + \frac{1}{120}y^5\frac{\partial^4 f}{\partial x^4} - \ldots \quad . \quad . \quad . \quad (4)$$

which set of equations satisfies for the interior of the fluid all the conditions of the problem, whilst at the same time it is easy to see that for *long* waves these series are rapidly convergent. Indeed, for such waves the state of motion changes slowly with x, and therefore the successive differential-quotients with respect to this variable of all functions referring, as f does, to the state of motion, must rapidly decrease.

Passing now to the conditions at the boundary, let p_1 (a constant) be the atmospheric pressure, p_1' the pressure at a point below the surface where the capillary forces cease to act, and T the surface-tension. We then have, distinguishing here and elsewhere by the suffix ($_1$) those quantities which refer to the surface,

$$p_1' = p_1 - \mathrm{T}\frac{\partial^2 y_1}{\partial x^2}\,;$$

but, according to a well-known equation of hydrodynamics,

$$\frac{p_1'}{\rho} = \chi(t) - \frac{\partial \phi_1}{\partial t} - \tfrac{1}{2}(u_1^2 + v_1^2) - gy_1,$$

therefore

$$\frac{p_1}{\rho} = \chi(t) - \frac{d\phi_1}{dt} - \tfrac{1}{2}(u_1^2 + v_1^2) - gy_1 + \frac{\mathrm{T}}{\rho}\frac{\partial^2 y_1}{\partial x^2} = \mathrm{L} - gy_1 + \mathrm{M}y_1^2$$
$$+ \mathrm{N}y_1^4 + \mathrm{P}y_1^6 + \ldots + \frac{\mathrm{T}}{\rho}\frac{\partial^2 y_1}{\partial x^2}, \quad . \quad (5)$$

where

$$L=\chi(t)-\int\frac{\partial f}{\partial t}dx-\tfrac{1}{2}f^2,$$

$$M=\frac{1}{2}f\frac{\partial^2 f}{\partial x^2}+\frac{1}{2}\frac{\partial^2 f}{\partial x\partial t}-\frac{1}{2}\left(\frac{\partial f}{\partial x}\right)^2,$$

$$N=-\frac{1}{24}f\frac{\partial^4 f}{\partial x^4}-\frac{1}{8}\left(\frac{\partial^2 f}{\partial x^2}\right)+\frac{1}{6}\frac{\partial f}{\partial x}\cdot\frac{\partial^3 f}{\partial x^3}-\frac{1}{24}\frac{\partial^4 f}{\partial x^3\partial t},$$

$$P=\frac{1}{720}f\frac{\partial^6 f}{\partial x^6}+\frac{1}{48}\frac{\partial^2 f}{\partial x^2}\cdot\frac{\partial^4 f}{\partial x^4}-\frac{1}{72}\left(\frac{\partial^3 f}{\partial x^3}\right)^2-\frac{1}{120}\frac{\partial f}{\partial x}\cdot\frac{\partial^5 f}{\partial x^5}+\frac{1}{720}\frac{\partial^6 f}{\partial x^5\partial t}.$$

By differentiation with respect to x equation (5) may be written

$$\frac{\partial L}{\partial x}+y_1^2\frac{\partial M}{\partial x}+y_1^4\frac{\partial N}{\partial x}+y_1^6\frac{\partial P}{\partial x}+\ldots-g\frac{\partial y_1}{\partial x}+2My_1\frac{\partial y_1}{\partial x}$$
$$+4Ny_1^3\frac{\partial y_1}{\partial x}+6Py_1^5\frac{\partial y_1}{\partial x}+\ldots+\frac{T}{\rho}\frac{\partial^3 y_1}{\partial x^3}=0. \quad . \quad (6)$$

Moreover, a second equation must hold good at the surface, viz.

$$-u_1\frac{\partial y_1}{\partial x}+v_1-\frac{\partial y_1}{\partial t}=0. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In order to satisfy equations (6) and (7) by the method of successive approximations, we put $y_1=l+\eta$, $f=q_0+\beta$, where l and q_0 are supposed to be constants, and η and β small functions depending upon x and t. Dealing, then, with the fact that for long waves, whose wave-length is great in comparison with the depth of the canal, every new differentiation with respect to x gives rise to continually smaller quantities, these equations become as a *first* approximation:—

$$q_0\frac{\partial\beta}{\partial x}+\frac{\partial\beta}{\partial t}+g\frac{\partial\eta}{\partial x}=0,$$

$$q_0\frac{\partial\eta}{\partial x}+\frac{\partial\eta}{\partial t}+l\frac{\partial\beta}{\partial x}=0,$$

and are satisfied by taking

$$\frac{d\eta}{dt}=\frac{d\beta}{dt}=0\,;\quad \beta=-\frac{q_0}{l}(\eta+\alpha),$$

and

$$q_0=\sqrt{gl}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where α is an arbitrary constant which we will suppose to be small.

It is obvious that this solution coincides with the one usually given for the case of long waves of arbitrary shape made stationary by attributing to the fluid a velocity equal and opposite to that of the waves, on the assumption that the velocity in a vertical direction may be neglected and that the horizontal velocity may be considered uniform across each section of the canal.

But, if we wish to proceed to a *second* approximation, we have to put

$$f=q_0-\frac{q_0}{l}(\eta+\alpha+\gamma) \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where γ is small compared with η and α. On substituting this in (6) and (7) and on writing out the result, rejecting all terms* which are small compared with any one of the remaining terms, we find respectively :—

$$\frac{q_0}{l}\frac{\partial\eta}{\partial t}+g\frac{\partial\gamma}{\partial x}-\frac{g}{l}(\eta+\alpha)\frac{\partial\eta}{\partial x}-\left(\tfrac{1}{2}\,l^2g-\frac{\mathrm{T}}{\rho}\right)\frac{\partial^3\eta}{\partial x^3}=0, \quad . \quad (10)$$

and

$$\frac{q_0}{l}\frac{\partial\eta}{\partial t}-g\frac{\partial\gamma}{\partial x}-\frac{g}{l}(2\eta+\alpha)\frac{\partial\eta}{\partial x}+\tfrac{1}{6}\,l^2g\frac{\partial^3\eta}{\partial x^3}=0. \quad . \quad . \quad (11)$$

In eliminating $\frac{\partial\gamma}{\partial x}$ from these equations, we have at last

$$\frac{d\eta}{dt}=\frac{3q_0}{2l}\frac{\partial\left(\frac{1}{2}\eta^2+\frac{2}{3}\alpha\eta+\frac{1}{3}\sigma\frac{\partial^2\eta}{\partial x^2}\right)}{\partial x} \quad . \quad . \quad . \quad (12)$$

where

$$\sigma=\tfrac{1}{3}l^3-\frac{\mathrm{T}l}{\rho g}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

This very important equation, to which we shall have frequently to revert in the course of this paper, indicates the deformation of a system of waves of arbitrary shape, but moving in one direction only. Before applying it, we may point out the close connexion between the constant α, which may still be chosen arbitrarily, and the uniform velocity given to the fluid. Indeed it is easy to see from (1) and (9) how a variation $\delta\alpha$ of the constant α corresponds to a change

---

* The terms for instance with $\frac{\partial\eta}{\partial x}\cdot\frac{\partial^2\eta}{\partial x^2}$ and $\left(\frac{\partial\eta}{\partial x}\right)^3$ are rejected in comparison with $\eta\frac{\partial\eta}{\partial x}$, which is retained in the equations, those with $\frac{\partial\gamma}{\partial t}$ and $\frac{\partial^3\eta}{\partial x^2\partial t}$ against $\frac{d\eta}{dt}$.

$\delta q = -\frac{q_0}{l}\delta\alpha$ in this velocity, but, on taking the variation of (12) with respect to α, we obtain

$$\delta\frac{d\eta}{dt} = \frac{q_0}{l}\,.\,\delta\alpha\,.\,\frac{\partial\eta}{\partial x} = -\delta q\,.\,\frac{\partial\eta}{\partial x},$$

which equation may be easily verified geometrically.

II. *Stationary Waves.*

For stationary waves $\frac{d\eta}{dt}$ must be zero. Therefore we have from (12)

$$\partial\left(\tfrac{1}{2}\eta^2 + \tfrac{2}{3}\alpha\eta + \tfrac{1}{3}\sigma\frac{\partial^2\eta}{\partial x^2}\right) = 0.$$

This gives by integration

$$c_1 + \tfrac{1}{2}\eta^2 + \tfrac{2}{3}\alpha\eta + \tfrac{1}{3}\sigma\frac{\partial^2\eta}{\partial x^2} = 0\,; \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and by multiplication with $6\,d\eta$ and further integration,

$$c_2 + 6c_1\eta + \eta^3 + 2\alpha\eta^2 + \sigma\left(\frac{\partial\eta}{\partial x}\right)^2 = 0. \quad . \quad . \quad . \quad (15)$$

If now the fluid be undisturbed at infinity, and if l be taken equal to the depth which it has there, then equations (14) and (15) must be satisfied by $\eta = 0$, $\frac{\partial\eta}{\partial x} = 0$, and $\frac{\partial^2\eta}{\partial x^2} = 0$. Therefore, in *this* case c_1 and c_2 are equal to zero, and equation (15) leads to

$$\frac{\partial\eta}{\partial x} = \pm\sqrt{-\frac{\eta^2(\eta + 2\alpha)}{\sigma}}. \quad . \quad . \quad . \quad . \quad (16)$$

Here, before we can proceed, we have to discriminate between σ positive and σ negative. In the *first case* 2α is necessarily negative because $\frac{\partial\eta}{\partial x}$ must be real for small values of η. If, then, we put it equal to $-h$, we have

$$\frac{d\eta}{dx} = \pm\sqrt{\frac{1}{\sigma}}\,.\,\eta\,.\,\sqrt{h - \eta}:$$

from which, supposing x to be zero for $\eta = h$, we easily obtain the well-known equation of the *positive* solitary wave, viz.:—

$$\eta = h\,\mathrm{sech}^2.\,x\sqrt{\frac{h}{4\sigma}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

In the *second case* 2α must be positive. In putting it equal to h, and in substituting $-\eta'$ for η, we have from (16)

$$\frac{\partial \eta'}{\partial x} = \pm\sqrt{\frac{1}{-\sigma}}\cdot\eta'\sqrt{h-\eta'},$$

or, by integration,

$$\eta = -\eta' = -h\,\mathrm{sech}^2\, x\sqrt{\frac{h}{-4\sigma}}.$$

This is the equation of a *negative* solitary wave, and we are able now to draw the conclusion that whenever σ is negative; that is whenever the depth of the liquid is less than $\sqrt{\frac{3T}{g\rho}}$, the stationary wave is a negative one. For water at 20° C. this limiting depth is equal to 0·47 cm. ($T=72$, $g=981$, $\rho=0{\cdot}998$ B.A.U.).

Now, for a further discussion of equation (15), we drop the assumption that the fluid is undisturbed at infinity. If then l be taken equal to the smallest depth of the liquid, we must have $\frac{\partial \eta}{\partial x}=0$ for $\eta=0$, and therefore in virtue of (15) $c_2=0$. On supposing then σ positive*, c_1 must be negative in order that $\frac{\partial \eta}{\partial x}$ may be real for small positive values of η, but then the equation

$$\eta^2+2\alpha\eta+6c_1=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

has a positive root h and a negative $-k$, and we may get from (15)

$$\frac{\partial \eta}{\partial x} = \pm\sqrt{\frac{1}{\sigma}\eta(h-\eta)(k+\eta)}. \quad . \quad . \quad . \quad (19)$$

By substitution in this equation (19) of $\eta = h\cos^2\chi$ and by integration, we find

$$\eta = h\,\mathrm{cn}^2\, x\sqrt{\frac{h+k}{4\sigma}}\left(M=\sqrt{\frac{h}{h+k}}\right), \quad . \quad . \quad (20)$$

---

* When σ negative, let then l be equal to the *greatest* depth. On substituting $\sigma=-\sigma'$, $\eta=-\eta'$ we have again c_1 negative,

$$\left(\frac{d\eta'}{dx}\right)^2 = \frac{1}{\sigma'}\,\eta'(h-\eta')(k+\eta'),$$

and, finally,

$$\eta=-\eta'=-h\,\mathrm{cn}^2\, x\sqrt{\frac{h+k}{4\sigma'}},$$

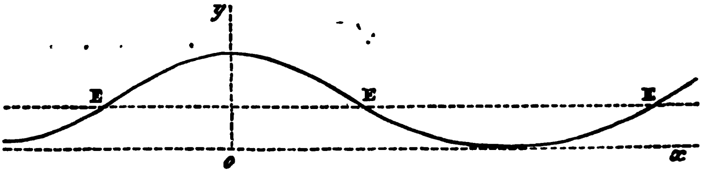
where h and $-k$ are the roots of $\eta'^2-2\alpha\eta+6c_1=0$.

which is the equation of a train of periodic waves whose wave-length increases when k decreases.

For $k=0$ this length becomes infinite, and the equation may be shown to coincide with (17).

The following figure (fig. 1) represents such a train of stationary waves for the case in which $k=\frac{9}{16}h$, $\mathrm{M}=0{\cdot}8$.

Fig. 1.



III. *Stationary Periodic Waves (Cnoidal Waves).*

Proceeding now to a further investigation of the waves determined by equation (20), we calculate from (10) and (11) the value of γ. From these equations we get

$$\frac{d\gamma}{dx}=-\frac{1}{2l}\eta\frac{\partial\eta}{\partial x}+\left(\frac{1}{3}l^2-\frac{\mathrm{T}}{2g\rho}\right)\frac{\partial^3\eta}{\partial x^3},$$

or by integration,

$$\gamma=-\frac{1}{4l}\eta^2+\left(\frac{1}{3}l^2-\frac{\mathrm{T}}{2g\rho}\right)\frac{\partial^2\eta}{\partial x^2},$$

where the constant of integration is rejected because its retention would only have had the effect of augmenting in equation (9) the value of the arbitrary constant α.

On substituting, then, f from (9) in (1) and (2), observing that in virtue of (14)

$$\frac{\partial^2\eta}{\partial x^2}=-\frac{1}{2\sigma}(3\eta^2+4\alpha\eta+6c_1)=-\frac{1}{2\sigma}(3\eta^2-2(h-k)\eta-hk),$$

these equations are replaced by

$$u=\sqrt{gl}-\sqrt{\frac{g}{l}}\left\{\eta+\tfrac{1}{2}(k-h)-\frac{\eta^2}{4l}+\left(\frac{1}{l}+\frac{\mathrm{T}}{2g\rho\sigma}\right)\left[(h-k)\eta\right.\right.$$

$$\left.\left.+\tfrac{1}{2}kh-\tfrac{3}{2}\eta^2\right]\right\}+\frac{1}{2\sigma}\sqrt{\frac{g}{l}}\{(h-k)\eta+\tfrac{1}{2}hk-\tfrac{3}{2}\eta^2\}y^2+\ldots . \quad (21)$$

$$v=\sqrt{\frac{g\eta(h-\eta)(k+\eta)}{l\sigma}}.y. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

When $k=0$ they determine the motion of the fluid for a solitary wave.

In the first place we now will endeavour to calculate the velocity of propagation. For the solitary wave this is simple enough. If we consider that the liquid at infinity is brought to rest when a uniform motion with a horizontal velocity

$$-q=-\sqrt{gl}\left(1+\frac{h}{2l}\right) \quad . \quad . \quad . \quad . \quad . \quad (23)$$

is added to the motion expressed by (21) and (22), it is clear that this velocity, with reversed sign, must be taken for the velocity of propagation of the solitary wave.

But for a train of oscillatory waves Sir G. Stokes has shown * that various definitions of this velocity may be given, leading at the higher order of approximation to different values. It seemed to us most rational to define it as the velocity of propagation of the wave-form when the *horizontal momentum* of the liquid has been reduced to zero by the addition of a uniform motion. This definition corresponds to the second one of Sir G. Stokes. According to it, we have to solve the equation

$$\int_0^\lambda dx \int_0^{l+\eta} (u-q)dy=0, \quad . \quad . \quad . \quad . \quad (24)$$

where q denotes the velocity of propagation, and where

$$\lambda=\frac{2K\sqrt{\sigma}}{\sqrt{h+k}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

is equal to the wave-length.

If, then,

$$V=\int_0^\lambda \eta dx=4\sqrt{\frac{\sigma}{h+k}}\left\{(h+k)E(K)-kK\right\}$$

$$=\lambda\left\{(h+k)\frac{E(K)}{K}-k\right\} \quad . \quad . \quad . \quad (26)$$

denote the volume of a single wave reckoned from above its lowest point, we get from (24), retaining only such terms as are of the first order compared with η, h, and k:—

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* Math. and Phys. Papers, vol. i. p. 202.

$$q=\frac{\int_0^\lambda dx\int_0^{l+\eta}u\,dy}{\int_0^\lambda dx\int_0^{l+\eta}dy}=\frac{\int_0^\lambda\left\{\sqrt{gl}-\sqrt{\frac{g}{l}}\eta-\frac{1}{2}(k-h)\sqrt{\frac{g}{l}}\right\}(l+\eta)dx}{\int_0^\lambda(l+\eta)dx}$$

$$=\frac{\sqrt{gl}\left(1-\frac{k-h}{2l}\right)l\lambda}{l\lambda+\mathrm{V}}=\sqrt{gh}\left(1-\frac{k-h}{2l}-\frac{\mathrm{V}}{l\lambda}\right)$$

$$=\sqrt{gl}\left(1+\frac{k+h}{2l}-\frac{k+h}{l}\frac{\mathrm{E(K)}}{\mathrm{K}}\right).\quad.\quad.\quad.\quad.\quad.\qquad(27)$$

On subtracting this velocity from that expressed by equation (21), we obtain

$$u'=u-q=-\sqrt{\frac{g}{l}}\left(\eta+k-(k+h)\frac{\mathrm{E}(k)}{\mathrm{K}}\right)=-\sqrt{\frac{g}{l}}\left(\eta-\frac{\mathrm{V}}{l}\right);\ (28)$$

and it is obvious at once that in this manner we have annulled the velocity of the particles for which

$$\eta=\frac{\mathrm{V}}{l}.$$

This last equation has a simple geometrical meaning. It designates those particles E (fig. 1) whose height above the bottom of the channel is equal to the height where the surface of the liquid would stand when the waves were flattened. Therefore for a first approximation we may say that the various particles of the fluid change the direction of their horizontal motion at the very moment when one of these points E is passing over them.

. . . . . .

We now proceed to the calculation of the path of a single particle of fluid. Let x_0, y_0 denote the coordinates of such a particle at the origin of time, and $x'=x_0+\xi'$, $y'=y_0+\zeta'$ its coordinates at the time t, u' and v' its horizontal and vertical velocity at that time, $l+\eta'$ its elevation above the bottom, then we have .

$$\xi'=\int_0^t u'dt=\sqrt{\frac{g}{l}}\int_0^t\left(\eta'-\frac{\mathrm{V}}{\lambda}\right)dt;$$

$$\zeta'=\int_0^t v'dt=\sqrt{\frac{g}{l}}\int_0^t y\frac{\partial\eta'}{\partial x'}dt.$$

Here η' is equal to the value of η for $x=x'+qt$; and therefore we have $dx=(u'-q)dt$, or to a first approximation $dt=-\frac{1}{q}dx=-\frac{1}{\sqrt{gl}}dx$; but then

$$\xi'=-\frac{1}{l}\int_{x_0}^{x_0+\sqrt{gl}\,.\,t}\left(\eta-\frac{V}{\lambda}\right)dx=\frac{Vt}{\lambda}\sqrt{\frac{g}{l}}-\frac{h}{l}\int_{x_0}^{x_0+\sqrt{gl}\,.\,t}\text{cn}^2\,\frac{2Kx}{\lambda}\,dx.$$

Or, according to a well-known formula *,

$$\xi'=-\frac{(h+k)\lambda}{2Kl}\left[Z\left(\frac{2K(x_0+\sqrt{gl}\,.\,t)}{\lambda}\right)-Z\left(\frac{2Kx_0}{\lambda}\right)\right]. \quad . \quad (29)$$

At the same time we have

$$\zeta=-\frac{1}{l}\cdot y\cdot\int_{x_0}^{x_0+\sqrt{gl}\,.\,t}\frac{\partial\eta}{\partial x}dx=-\frac{h}{l}\cdot y\cdot\left[\text{cn}^2(x_0+\sqrt{gl}\,.\,t)\sqrt{\frac{h+k}{4\sigma}}\right.$$
$$\left.-\text{cn}^2\,x_0\sqrt{\frac{h+k}{4\sigma}}\right]. \quad . \quad . \quad . \quad . \quad (30)$$

Of course, as all fluid particles with the same y describe congruent paths, these formulæ may be simplified by supposing $x_0=0$.

IV. *Deformation of Non-Stationary Waves.*

In order to study the deformation of non-stationary waves, we will now apply our formula (12) to various types of waves.

Solitary Waves.—As a first example we choose a solitary wave whose surface is given by

$$\eta=h\,\text{sech}^2\,px. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

According to (12), the deformation of this wave is expressed by

$$\frac{d\eta}{dt}=-\frac{3q_0ph}{l}(4\sigma p^2-h)\left[-\text{sech}^2\,px\right.$$
$$\left.+\frac{2(\alpha+2\sigma p^2)}{3(4\sigma p^2-h)}\right]\text{sech}^2\,px\,.\,\tanh px. \quad . \quad . \quad (32)$$

But before we are able to draw any conclusion from this expression, it is necessary to separate the two parts of $\frac{d\eta}{dt}$, of which the first is due to a true change of form of the wave-surface, whilst the second may be attributed to a small advancing motion of the wave, which is left after the addition of the uniform motion with velocity $q_0=\sqrt{gl}$. To this effect we have still at our disposal the quantity α, whose close connexion with the uniform motion, which we have added in order to make the wave nearly stationary, has been indicated above.

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* $Z(u)=u\left(1-\frac{E(K)}{K}\right)-M^2\int_0^u \text{sn}^2\,u\,.\,du$. Compare, for instance, Cayley, 'An Elementary Treatise on Elliptic Functions,' 1876, ch. vi. § 187.

One of the best ways to obtain the desired separation is certainly to make stationary the highest point of the wave, and this is effected by fulfilling the condition

$$2(\alpha+2\sigma p^2)=3(4\sigma p^2-h),$$

or

$$\alpha=4\sigma p^2-\tfrac{3}{2}h\,;$$

for in that case equation (32) is simplified to

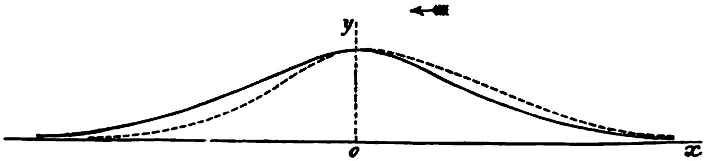
$$\frac{d\eta}{dt}=-\frac{3q_0ph}{l}(4\sigma p^2-h)\,\mathrm{sech}^2\,px\,.\,\tanh^3 px\,; \quad . \quad (33)$$

and then, for $x=0$,

$$\frac{\partial\cdot\dfrac{\partial\eta}{\partial x}}{\partial t}=\frac{\partial\cdot\dfrac{\partial\eta}{\partial t}}{\partial x} \text{ is zero together with } \frac{\partial\eta}{\partial x}.$$

In discussing this equation (33), we see at once that a solitary wave (31) is stationary when $h=4\sigma p^2$; and this is in accordance with the equation (17) of the stationary solitary wave which we have obtained above. When $h>4\sigma p^2$, the change of form of the wave, calculated from (33), is shown by the dotted line in fig. 2.

Fig. 2.



Here the wave becomes steeper in front*, whilst for $h<4\sigma p^2$ the figure would show the opposite change of form, when, contrary to the opinion expressed by Airy and others, the wave becomes less steep in front and steeper behind.

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[*] The left side of the figure is the front side of the wave, because the wave has been made stationary by the application of a positive velocity (*i. e.* from left to right) to the fluid.

If, now, we take account of the fact that, as may easily be inferred from (31), the wave-surface becomes steeper in proportion as p is increased, we are then justified in saying that a solitary wave which is *steeper* than the stationary one, corresponding to the same height, becomes less steep *in front* and steeper *behind*, but that its behaviour is exactly opposite when it is *less steep* than the stationary one.

Cnoidal Waves.—Applying formula (12) to the cnoidal wave,

$$\eta = h\,\mathrm{cn}^2 px, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (34)$$

we get

$$\frac{d\eta}{dt} = -\frac{3q_0ph}{l}\left\{\frac{2[\alpha-\sigma p^2(2-4\mathrm{M}^2)]}{3(4\sigma\mathrm{M}^2p^2-h)} - \mathrm{cn}^2.px\right\}(4\sigma\mathrm{M}^2p^2 - h)\,\mathrm{sn}\,px\,.\,\mathrm{cn}\,px\,.\,\mathrm{dn}\,px. \quad . \quad . \quad . \qquad (35)$$

Supposing then

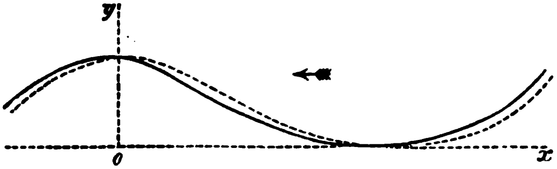
$$2[\alpha-\sigma p^2(2-4\mathrm{M}^2)] = 3(4\sigma\mathrm{M}^2p^2-h),$$

we have

$$\frac{d\eta}{dt} = -\frac{3q_0ph}{l}(4\sigma\mathrm{M}^2p^2-h)\,\mathrm{sn}^3px\,.\,\mathrm{cn}\,px\,.\,\mathrm{dn}\,px. \qquad (36)$$

Here fig. 3 shows the change of form calculated for the case $h-4\sigma\mathrm{M}^2p^2>0$.

Fig. 3.



When $h-4\sigma\mathrm{M}^2p^2=0$, the waves are stationary in accordance with (20), whilst for $h-4\sigma\mathrm{M}^2p^2<0$ they become steeper *behind*; and this last result, since p is inversely proportional to the wave-length, may be stated by saying that cnoidal waves become less steep in front and steeper behind when, for a given modulus and a given height, their length is smaller than the one required for the stationary wave of this modulus and height.

In proportion as M is taken smaller the cnoidal waves more and more resemble sinusoidal waves. They would take the sinusoidal form for $\mathrm{M}=0$, but then an infinitely small wave-length would be required for the stationary case. For this reason sinusoidal waves may always be considered as cnoidal waves whose length is too large to be stationary, that is, they are always becoming steeper in front.

Sinusoidal Waves.—This last result is easily verified by direct application of (12) to the equation of a train of sinusoidal waves:

$$\eta = \mathrm{A}\sin\frac{2\pi x}{\lambda};$$

for, supposing

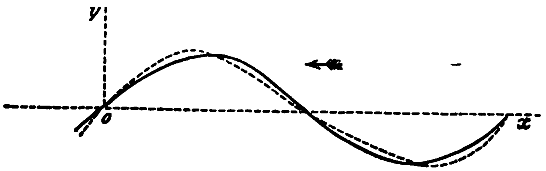
$$\alpha = \frac{2\pi^2\sigma}{\lambda^2},$$

we obtain

$$\frac{d\eta}{dt} = \frac{3q_0\pi\mathrm{A}^2}{2l\lambda}\sin\frac{4\pi x}{\lambda};$$

and from this the change of form indicated in fig. 4 is easily calculated.

Fig. 4.



More complicated Cases.—For the sake of curiosity, we represent by means of the following figures the change of form for some more complicated cases.

Fig. 5.

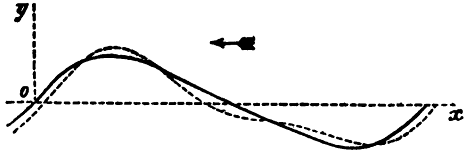


Fig. 6.

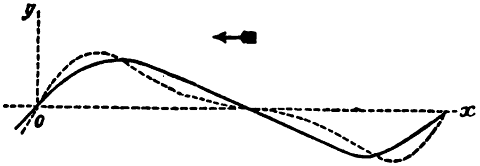
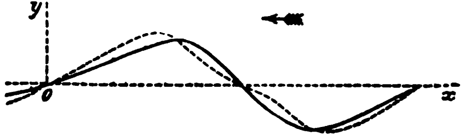


Fig. 7.



Figs. 5 and 6 refer to the equation

$$\eta = A_1 \sin\frac{2\pi x}{\lambda} + \tfrac{1}{3}A_1 \sin\frac{4\pi x}{\lambda}.$$

In fig. 5 $\frac{A_1}{l}$ is supposed to be small compared with $\left(\frac{l}{\lambda}\right)^2$, as is the case with waves of extremely small height. In fig. 6 we suppose $\left(\frac{l}{\lambda}\right)^2$ to be small in regard to $\frac{A_1}{l}$. Generally for more complicated forms of wave these two cases have to be discriminated. When there is a moderate proportionality between the two fractions the result is still more complicated.

Finally, fig. 7 refers to the equation

$$\eta = A_1 \sin\frac{2\pi x}{\lambda} - \tfrac{1}{3}A_1 \sin\frac{4\pi x}{\lambda},$$

in case that $\left(\frac{l}{\lambda}\right)^2$ is the smaller fraction.

It is worthy of remark that all these waves grow steeper in front.

V. *Calculation of the Fluid Motion for Stationary Waves to the Higher Order of Approximation.*

In order to remove every doubt as to the existence of absolutely stationary waves, we will show how by development in rapidly convergent series the state of motion of the fluid belonging to such a wave-motion may be calculated.

Expressing again the horizontal and vertical velocity of a particle by means of the series (1) and (2) which fulfil all the conditions for the interior of the fluid, we have only, neglecting capillarity, to satisfy the surface-conditions,

$$v_1 = u_1 \frac{\partial \eta}{\partial x}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

and

$$u_1^2 + v_1^2 + 2g\eta = \text{constant}. \quad . \quad . \quad . \quad . \quad . \quad (38)$$

For the case of cnoidal waves, which is the general one, we have found as a first approximation,

$$\left(\frac{\partial \eta}{\partial x}\right)^2 = \frac{3}{l^3}\eta(h-\eta)(k+\eta).$$

But now, to obtain higher approximations, we assume, indicating by accents differentiation with respect to x,

$$\eta'^2 = a\eta(h-\eta)(k+\eta)(1+b\eta+c\eta^2+\ldots), \quad . \quad . \quad (39)$$

and

$$f = q + r\eta + s\eta^2 + t\eta^3 + u\eta^4 + \ldots \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

On writing out (39), neglecting such terms as are of a higher order than the fourth compared with η, h, and k, which latter quantities are of the same order, we obtain

$$\eta'^2 = ahk\eta + \{a(h-k) + abhk\}\eta^2 + \{-a + ab(h-k)\}\eta^3 - ab\eta^4; \quad . \quad (41)$$

and by differentiation,

$$\eta'' = \tfrac{1}{2}ahk + \{a(h-k) + abhk\}\eta + \{-\tfrac{3}{2}a + \tfrac{3}{2}ab(h-k)\}\eta^2 - 2ab\eta^3. \quad (42)$$

From (40), by successive differentiations and substitutions, retaining all terms up to the third and the $3\frac{1}{2}$th order, we deduce :—

$$f' = (r + 2s\eta + 3t\eta^2)\eta';$$

$$f'' = \tfrac{1}{2}arhk + \{ar(h-k) + abrhk + 3ashk\}\eta$$
$$+ \{-\tfrac{3}{2}ar + \tfrac{3}{2}abr(h-k) + 4as(h-k)\}\eta^2 + (-2abr - 5as)\eta^3;$$

$$f''' = [ar(h-k) + abrhk + 3ashk$$
$$+ \{-3ar + 3abr(h-k) + 8as(h-k)\}\eta + (-6abr - 15as)\eta^2]\eta';$$

$$f^{\text{iv}} = \tfrac{1}{2}a^2rhk(h-k) + \{a^2r(h-k)^2 - \tfrac{3}{2}a^2rhk\}\eta$$
$$- \tfrac{15}{2}a^2r(h-k)\eta^2 + \tfrac{15}{2}a^2r\eta^3;$$

$$f^{\text{v}} = [a^2r(h-k)^2 - \tfrac{3}{2}a^2rhk - 15a^2r(h-k)\eta + \tfrac{45}{2}a^2r\eta^2]\eta';$$

where η' is a quantity of the order $\frac{3}{2}$.

Substituting these values in equation (1), where $y = l + \eta$, we have, retaining terms of the third order :—

$$u_1 = f - \tfrac{1}{2}l^2f'' - l\eta f'' + \tfrac{1}{24}l^4f^{\text{iv}} = q - \tfrac{1}{4}arl^2hk + \tfrac{1}{48}a^2rl^4hk(h-k)$$
$$+ \{r - \tfrac{1}{2}arl^2(h-k) - \tfrac{1}{2}abrl^2hk - \tfrac{3}{2}asl^2hk - \tfrac{1}{2}arlhk$$
$$+ \tfrac{1}{24}a^2rl^4(h-k)^2 - \tfrac{3}{16}a^2rl^4hk\}\eta$$
$$+ \{s + \tfrac{3}{4}al^2r - \tfrac{3}{4}abrl^2(h-k) - 2asl^2(h-k)$$
$$- arl(h-k) - \tfrac{5}{16}a^2rl^4(h-k)\}\eta^2$$
$$+ \{t + abrl^2 + \tfrac{5}{2}asl^2 + \tfrac{3}{2}arl + \tfrac{5}{16}a^2rl^4\}\eta^3. \quad . \quad . \quad . \quad . \quad (43)$$

We find in the same way, including terms of the $3\frac{1}{2}$th order :—

$$v_1 = -lf' - \eta f' + \tfrac{1}{6}l^3f''' + \tfrac{1}{2}l^2\eta f''' - \tfrac{1}{120}l^5f^{\text{v}}$$
$$= \eta'[-rl + \tfrac{1}{6}arl^3(h-k) + \tfrac{1}{6}abrl^3hk + \tfrac{1}{2}asl^3hk - \tfrac{1}{120}a^2rl^5(h-k)^2$$
$$+ \tfrac{3}{80}a^2rl^5hk + \{-2sl - r - \tfrac{1}{2}arl^3 + \tfrac{1}{2}abrl^3(h-k)$$
$$+ \tfrac{4}{3}asl^3(h-k) + \tfrac{1}{2}arl^2(h-k) + \tfrac{1}{8}a^2rl^5(h-k)\}\eta$$
$$+ \{-3tl - 2s - abrl^3 - \tfrac{5}{2}asl^3 - \tfrac{3}{2}arl^2 - \tfrac{3}{16}a^2rl^5\}\eta^2]. \quad . \quad (44)$$

If now we write, in accordance with (37),

$$u_1 = \frac{v_1}{\eta'} = \mathrm{A} + \mathrm{B}\eta + \mathrm{C}\eta^2 + \mathrm{D}\eta^3 + \ldots, \quad . \quad . \quad . \quad (45)$$

we have from (43) and (44):—

$$\mathrm{A} = q - \tfrac{1}{4}arl^2hk + \tfrac{1}{48}a^2rl^4hk(h-k) = -rl + \tfrac{1}{6}arl^3(h-k)$$
$$+ \tfrac{1}{6}abrl^3hk + \tfrac{1}{2}asl^3hk - \tfrac{1}{120}a^2rl^5(h-k)^2 + \tfrac{3}{80}a^2rl^5hk. \quad . \quad (46)$$

$$\mathrm{B} = r - \tfrac{1}{2}arl^2(h-k) - \tfrac{1}{2}abrl^2hk - \tfrac{3}{2}asl^2hk - \tfrac{1}{2}arlhk$$
$$+ \tfrac{1}{24}a^2rl^4(h-k)^2 - \tfrac{3}{16}a^2rl^4hk = -2sl - r - \tfrac{1}{2}arl^3$$
$$+ \tfrac{1}{2}abrl^3(h-k) + \tfrac{4}{3}asl^3(h-k) + \tfrac{1}{2}arl^2(h-k) + \tfrac{1}{8}a^2rl^5(h-k). \quad (47)$$

$$\mathrm{C} = s + \tfrac{3}{4}al^2r - \tfrac{3}{4}abrl^2(h-k) - 2asl^2(h-k) - arl(h-k) - \tfrac{5}{16}a^2rl^4(h-k)$$
$$= -3tl - 2s - abrl^3 - \tfrac{3}{2}asl^3 - \tfrac{3}{2}arl^2 - \tfrac{3}{16}a^2rl^5. \quad . \quad (48)$$

$$\mathrm{D} = t + abrl^2 + \tfrac{3}{2}asl^2 + \tfrac{3}{2}arl + \tfrac{5}{16}a^2rl^4. \quad . \quad . \quad . \quad . \quad . \quad . \quad (49)$$

Moreover, since (38) may be written in the form

$$u_1^2(1+\eta'^2) + 2g\eta = (\mathrm{A} + \mathrm{B}\eta + \mathrm{C}\eta^2 + \mathrm{D}\eta^3)^2(1 + ahk\eta$$
$$+ a(h-k)\eta^2 - a\eta^3) + 2g\eta = \text{constant}, \quad . \quad . \quad . \quad . \quad . \quad (50)$$

we readily obtain

$$2\mathrm{AB} + ahk\mathrm{A}^2 + 2g = 0, \quad . \quad . \quad . \quad . \quad (51)$$

$$2\mathrm{AC} + \mathrm{B}^2 + a(h-k)\mathrm{A}^2 = 0. \quad . \quad . \quad . \quad . \quad (52)$$

$$2\mathrm{AD} + 2\mathrm{BC} - a\mathrm{A}^2 = 0. \quad . \quad . \quad . \quad . \quad (53)$$

From the equations (46), (47), (48), (51), (52), (53), the six quantities q, r, s, t, a, and b may be calculated, and if we had retained everywhere terms of one higher order, we might have got eight equations with eight unknown quantities, &c.

By a first approximation we readily obtain from (46)–(49):—

$$r = -\frac{q}{l}; \quad s = \frac{q}{l^2} + \tfrac{1}{4}aql; \quad t = -\frac{q}{l^3} - \tfrac{1}{3}aq + \tfrac{1}{3}abql - \tfrac{7}{48}a^2ql^3;$$

$$\mathrm{A} = q; \quad \mathrm{B} = -\frac{q}{l}; \quad \mathrm{C} = \frac{q}{l^2} - \tfrac{1}{2}aql;$$

$$\mathrm{D} = -\frac{q}{l^3} + \tfrac{2}{3}aq - \tfrac{2}{3}abql + \tfrac{1}{6}a^2ql^3;$$

and then from (51)–(53),

$$q^2 = gl; \quad a = \frac{3}{l^3}; \quad b = \frac{3}{4l}. \quad . \quad . \quad . \quad . \quad . \quad (54)$$

Proceeding to the second approximation, we find

$$r=-\frac{q}{l}\left(1+\frac{h-k}{2l}\right);\quad s=\frac{q}{l^2}+\tfrac{1}{4}aql+\tfrac{7}{4}\frac{q}{l^2}\cdot\frac{h-k}{l};\quad \mathrm{A}=q;$$

$$\mathrm{B}=-\frac{q}{l}+\frac{q}{l}\cdot\frac{h-k}{l};\ \mathrm{C}=\frac{q}{l^2}-\tfrac{1}{2}aql-\frac{19}{8}\frac{q}{l^2}\cdot\frac{h-k}{l};$$

and then again from (51) and (52),

$$q^2=gl\left(1+\frac{h-k}{l}\right);\ a=\frac{3}{l^3}-\frac{15}{4}\cdot\frac{h-k}{l^4}.\quad .\quad .\quad (55)$$

Finally, a third approximation leads to :—

$$r=-\frac{q}{l}\left(1+\frac{h-k}{2l}-\frac{9}{20}\frac{(h-k)^2}{l^2}-\frac{93}{80}\frac{hk}{l^2}\right);\ \mathrm{A}=q+\tfrac{3}{4}q\cdot\frac{hk}{l^2};$$

$$\mathrm{B}=-\frac{q}{l}+\frac{q}{l}\cdot\frac{h-k}{l}-\frac{21}{20}\frac{q}{l}\frac{(h-k)^2}{l^2}-\frac{12}{5}\frac{q}{l}\cdot\frac{hk}{l^2};$$

$$q^2=gl\left(1+\frac{h-k}{l}-\frac{1}{20}\frac{(h-k)^2}{l^2}-\frac{33}{20}\frac{hk}{l^2}\right).\quad .\quad .\quad .\quad (56)$$

By means of these results we may now readily obtain from (1) and (2) expressions for u and v including respectively the terms of the 2nd and $2\frac{1}{2}$th order.

They are :—

$$u=\sqrt{gl}\left\{\left(1+\frac{h-k}{2l}-\frac{3}{20}\frac{(h-k)^2}{l^2}-\frac{33}{40}\frac{hk}{l^2}\right)+\left(1+\frac{h-k}{l}\right)\frac{\eta}{l}\right.$$
$$\left.+\frac{7}{4}\frac{\eta^2}{l^2}+\left(\frac{3}{4}\cdot\frac{hk}{l^2}+\frac{3}{2}\frac{h-k}{l}\frac{\eta}{l}-\frac{9}{4}\frac{\eta^2}{l^2}\right)y^2\right\}.\quad .\quad .\quad (57)$$

$$v=\eta'\sqrt{\frac{g}{l}}\left\{\left(1+\frac{h-k}{l}-\frac{7}{4}\cdot\frac{\eta}{l}\right)y+\left(-\frac{h-k}{2l}+\frac{3}{2}\cdot\frac{\eta}{l}\right)y^3\right\};\ (58)$$

where

$$\eta'^2=\frac{3}{l^3}\left(1-\frac{5}{4}\frac{h-k}{l}\right)(h-\eta)(k+\eta)\left(1+\frac{3}{4}\cdot\frac{\eta}{l}\right).\quad .\quad (59)$$

VI. *Calculation of the Equation of the Surface.*

We will now show how for the equation of the surface of a stationary train of waves a more correct expression than (20) can be deduced. For this purpose we have to integrate the differential equation (39), or rather we have to prove that a series can be given which solves this equation to any desired degree of accuracy. Now such a series may be obtained in the following manner. Let

$$\eta_1 = h_1 \operatorname{cn}^2 \tfrac{1}{2}x\sqrt{a(h_1+k_1)}\left(\mathrm{M}=\sqrt{\frac{h_1}{h_1+k_1}}\right) \quad . \quad (60)$$

represent the solution of an equation

$$\eta_1'^2 = a\eta_1(h_1-\eta_1)(k_1+\eta_1), \quad . \quad . \quad . \quad . \quad (61)$$

where h_1 and k_1 have values which are slightly different from those of h and k in (39); then these values and the coefficients α, β, &c., of a series

$$\eta = \alpha\eta_1 + \beta\eta_1^2 + \gamma\eta_1^3 + \delta\eta_1^4 + \ldots \quad . \quad . \quad (62)$$

may be determined in such a way* that this series (62) satisfies the equation (39).

Indeed, substituting (62) in (39) and taking into account (61), equation (39) reduces to

$$\begin{aligned}(\alpha+2\beta\eta_1+3\gamma\eta_1^2+\ldots)^2(h_1-\eta_1)(k_1+\eta_1)\\ =(\alpha+\beta\eta_1+\gamma\eta_1^2+\ldots)(h-\alpha\eta_1-\beta\eta_1^2-\gamma\eta_1^3+\ldots)(k+\alpha\eta_1\\ +\beta\eta_1^2+\gamma\eta_1^3+\ldots)(1+b\alpha\eta_1+(b\beta+c\alpha)\eta_1^2+\ldots),\end{aligned}$$

and it is only necessary to equalize the coefficients of the corresponding terms of both members of this equation.

If we retain all terms to the fourth order, we find in this way, after some reductions :—

$$ah_1k_1 - hk = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (63)$$

$$\alpha^2(h_1-k_1) - \alpha^2(h-k) - (b\alpha^2-3\beta)hk = 0. \quad . \quad . \quad . \quad . \quad . \quad (64)$$

$$-\alpha^3+\alpha^4-(b\alpha^4-2\alpha^2\beta)(h-k)-(c\alpha^3-2b\alpha^2\beta+8\beta^2-5\alpha\gamma)hk=0 \quad (65)$$

$$-4a\beta+3a^2\beta+b\alpha^4-(c\alpha^3+3b\alpha^2\beta-3\beta^2-4\alpha\gamma)(h-k)=0 \quad . \quad . \quad (66)$$

$$-4\beta^2-6\alpha\gamma+c\alpha^4+4b\alpha^2\beta+3a\beta^2+3a^2\gamma=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (67)$$

To a *first* approximation these equations are satisfied by taking

$$h_1=h\,;\ k_1=k\,;\ \alpha=1\,;\ \beta=b\,;\ \gamma=b^2+\tfrac{1}{3}c \quad . \quad . \quad (68)$$

If then we substitute in (63), (64), (65), and (66)

$$h_1=h+\epsilon,\ \ k_1=k+\varpi,\ \ \alpha=1+\alpha_1,\ \ \beta=b+\beta_1$$

where α_1 and β_1 are quantities of the first, ϵ and ϖ of the second order, we find from these equations by *second* approximation:—

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* The coefficient a in (61) might also have been chosen slightly different in value from a in (39), but this would only have introduced an unnecessary indeterminateness in the solution.

$$\epsilon = -bhk\,;\quad \varpi = bhk\,;\quad \alpha_1 = -b(h-k)\,;\quad \beta_1 = (-2b^2 + \tfrac{1}{3}c)(h-k) \,.\,. \quad (69)$$

Substituting as a *third* approximation :—

$$h_1 = h - bhk + \epsilon_1\,;\quad k_1 = k + bhk + \varpi_1,\quad \alpha = 1 - b(h-k) + \alpha_2,$$

we obtain finally,

$$\epsilon_1 = \tfrac{1}{3}chk(-h+2k)\,;\quad \varpi_1 = \tfrac{1}{3}chk(2h-k)\,;\quad \alpha_2 = (b^2 - \tfrac{2}{3}c)(h^2 - hk + k^2) . \quad (70)$$

Hence the equation of the surface of the waves is, including all terms of the third order :—

$$\eta = [1 - b(h-k) + (b^2 - \tfrac{2}{3}c)(h^2 - hk + k^2)]\eta_1 + [b + (-2b^2 + \tfrac{1}{3}c)(h-k)]\eta_1{}^2 + (b^2 + \tfrac{1}{3}c)\eta_1{}^3 + \,.\quad . \quad (71)$$

where

$$\eta_1 = h_1 \operatorname{cn}^2 \tfrac{1}{2}x\sqrt{a(h_1+k_1)}\left(\mathrm{M} = \sqrt{\frac{h_1}{h_1+k_1}}\right) .\;.\;. \quad (60)$$

$$h_1 = h - bhk + \tfrac{1}{3}chk(-h+2k)\,;\quad k_1 = k + bhk + \tfrac{1}{3}chk(2h-k) . \quad (72)$$

Here, according to (59),

$$a = \frac{3}{l^3}\left(1 - \frac{5}{4}\,\frac{h-k}{l} + \ldots\right);\quad b = \frac{3}{4l} + \ldots\,;\;.\;. \quad (73)$$

whereas the value of c and more correct expressions for a and b could only have been obtained by means of still more tedious calculations, which we have not executed.

If we confine ourselves to that degree of approximation for which all the calculations have been effected, we may write for the equation of the wave-surface :—

$$\eta = \left[1 - \frac{3(h-k)}{4l}\right]\eta_1 + \frac{3}{4l}\eta_1{}^2 .\;.\;.\;.\;. \quad (74)$$

$$\eta_1 = h \operatorname{cn}^2 \tfrac{1}{2}\left(1 - \frac{5(h-k)}{8l}\right)x\sqrt{\frac{3(h+k)}{l^3}} .\;.\;. \quad (75)$$

$$\mathrm{M} = \left(1 - \frac{3k}{8l}\right)\sqrt{\frac{h}{h+k}} .\;.\;.\;.\;.\;. \quad (76)$$

For the solitary wave, when $k = 0$, we have *

$$\eta = \left[1 - \frac{3h}{4l}\right]\eta_1 + \frac{3}{4l}\eta_1{}^2 .\;.\;.\;.\;. \quad (77)$$

$$\eta_1 = h \operatorname{sech}^2 \tfrac{1}{2}\left(1 - \frac{5h}{8l}\right)x\sqrt{\frac{3h}{l^3}} .\;\;.\;. \quad (78)$$

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* Another close approximation of the surface-equation of this wave has been deduced by McCowan, Phil. Mag. [5] vol. xxxii. (1891), p. 48.

XLII. *The Tin-Chromic Chloride Cell.*

By S. Skinner, *M.A.*[*]

A CELL consisting of a tin and platinum couple in a solution of the green chromic chloride was described by W. E. Case in the Proc. R. S. 1886, p. 345. The tin is dissolved by the chromic chloride at a high temperature only, and when the solution is cooled the tin is precipitated. The chemical changes are represented by the following statement:—

$$Cr_2Cl_6 + Sn \rightleftharpoons SnCl_2 + 2CrCl_2.$$

As the reaction is reversed on cooling, the cell has the interesting feature that at the end of a hot and cold cycle it is in the same chemical condition as it was at the commencement. It thus offers a method of deriving electrical energy directly from heat. The author of the account gives a curve of electromotive force, and finds that it is zero at 60° F., and increases to about ¼ volt at 200° F. I shall show that the E.M.F. is not zero at the ordinary temperature, but is about ½ volt; however, the cell will not give any current at these temperatures on account of polarization. It appears that the curve given by Mr. Case is not an E.M.F. curve, but one which was probably obtained by using a wire voltmeter, and therefore really represents the current the cell is capable of producing.

The tin is precipitated in small crystals from the cooling solution of $CrCl_2$ and $SnCl_2$, and does not then form a satisfactory electrode. I have therefore arranged the cell with an amalgam of tin in place of the solid rod. The precipitated crystals fall into the mercury and dissolve so as to reconstitute a suitable electrode. My construction of the cell is very much like that of a Clark cell.

A test-tube with a platinum wire through the base has fluid amalgam in it, and this is covered with a solution of pure Cr_2Cl_6, made by dissolving violet sublimed Cr_2Cl_6 in water with the aid of a fragment of tinfoil. A platinum plate and wire form the positive pole of the cell.

Connecting such a cell at 15° C. with a galvanometer, there is a sudden deflexion which very rapidly becomes less until some small steady value is reached. On warming the cell the deflexion increases until it is relatively large. These observations show that the cell cannot produce a continuous current of any magnitude at low temperatures, but at high temperatures it does.

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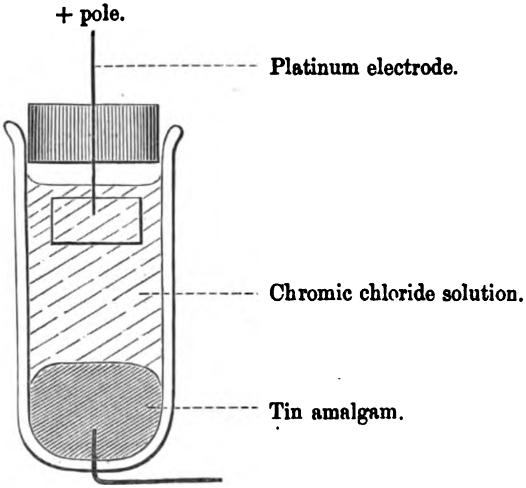

If the E.M.F. of the cell be measured on a potentiometer, or by means of a ballistic galvanometer and condenser, by either of which methods the cell is not called on to produce a current, it is found that the E.M.F. at all temperatures is approximately ½ volt, and that the E.M.F. is slightly less at the boiling-point of water than at the ordinary temperature.

The explanation of the results is not difficult. The cell polarizes very rapidly at low temperatures, and the opposing E.M.F. of polarization increases so rapidly and so largely that almost at the moment of connexion the effective E.M.F. becomes zero. The cell behaves like a condenser which is connected to a battery through a very high resistance. Such a condenser would discharge itself when its plates were connected, but when they were isolated again it would slowly become charged by the battery through the high resistance.

At the high temperature the polarization is very largely reduced, and the cell will produce a continuous current.

Another interesting feature of the cell is that it may be used as the mechanism of a heat-engine for the production of work, and we can trace in it the complete cycle of Carnot. Let the cell be placed in a hot chamber, and work may be derived from it until all the Cr_2Cl_6 or the tin is used. Then let the cell be placed in a cold chamber, it will give up heat, and becomes restored to its original chemical condition.

Measurements of the electromotive force of two cells are given in the following tables. The first cell contained tin-amalgam, and the second cell contained a tin rod. Both cells had not been used for producing current within the 24 hours immediately preceding the measurements.

Cell No. 1. Tin-amalgam.

Temperature.	E.M.F.
15·5° C.	·44 volt.
20·5	·45
49·0	·43
75·0	·41
93·0	·40
96·0	·40
97·0	·40
20·0	·44

Cell No. 2. Tin rod.

Temperature.	E.M.F.
16°	·52 volt.
30°	·52
97°	·45

Connexion was made and a current allowed to flow for 1 minute, and then the cell was allowed to rest for 1 minute :

97° | ·08 volt.

At end of second minute :

97° | ·11 volt.

At end of third minute :

97° | ·11 volt.

These results showed that the cell had polarized, and was only slowly recovering its electromotive force.

When a solution of the green chromic chloride at the ordinary temperature has silver nitrate added to it, only two-thirds of the chlorine is precipitated. This, according to the theory of ionisation, indicates that only two atoms out of three act as negative ions, the other atom apparently being part of the positive ion. On the other hand, if a solution of chromic chloride near 100° be treated with silver nitrate, the whole of the chlorine may be precipitated. This indicates that at the higher temperature all the chlorine atoms behave as negative ions.

Taking this into account, the Grotthus chain representing the action of the cell about 15° must be as follows :—

$$\mathrm{Pt} \mid \mathrm{ClCrCl_2} \mid \mathrm{ClCrCl_2} \mid \mathrm{ClCrCl_2} \mid \mathrm{Sn},$$

becoming, after connexion,

$$\mathrm{Pt,ClCr} \mid \mathrm{Cl_2ClCr} \mid \mathrm{Cl_2ClCr} \mid \mathrm{Cl_2Sn}.$$

This view of the action leaves the ion ClCr polarizing the cell. Now if a depolarizer acts so as to remove this ion, the cell will go on producing a current. The excess of chromic chloride might perform this function, forming with this ion chromous chloride :

$$\mathrm{CrCl} + \mathrm{CrCl_3} = 2\mathrm{CrCl_2}.$$

The behaviour of the cell shows that this does not take place readily.

A similar view of the action in the cell at about 100° indicates the presence of chromium ions as the polarizing agent. At this temperature there is not much polarization ; so that it appears the following chemical change takes place readily :

$$\mathrm{Cr} + 2\mathrm{CrCl_3} = 3\mathrm{CrCl_2}.$$

XLIII. *Some Acoustical Experiments.* *By* CHARLES V. BURTON, *D.Sc., Demonstrator in Physics, University College, London*[*].

I. *Subjective Lowering of Pitch.*

1. A YEAR or two ago, in the physical laboratory of Bedford College, London, the professor, Mr. Womack, called my attention to the fact that a tuning-fork which was being used by a student appeared to rise perceptibly in pitch as the vibration died away. It then occurred to me that the effect observed might be a subjective one : that one result of increasing the intensity of a musical note without changing its frequency, might be to depress the pitch as estimated by ear. To determine this point I have made experiments upon myself, and on others whose perception of musical intervals was known to be reliable.

2. Let a tuning-fork mounted on a resonance-box be strongly excited by bowing, and immediately let the open end of the resonance-box be brought very close to one ear, the other ear being preferably closed. After a second or so, let the fork and box be moved away from the ear and held at arm's length, then brought close to the ear again, and so on, backwards and forwards, two or three times. If there is any

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subjective depression of pitch accompanying increase of loudness without change of frequency, the fork will appear to be lower in pitch when close to the ear and higher when further away, the effect becoming less marked as the vibration gradually dies down. This is what observation shows to be actually the case, and it is evidently nothing of the nature of a Doppler effect with which we are here concerned. In the first place, the motion of the fork from one position to the other may be made quite slow; and in the second place, the difference of pitch is observed, *not* between the fork approaching and the fork receding, but between the nearer and further positions of the fork.

3. In some of these observations a fork giving the note c' (256 complete vibrations per second) has been used, the effect with forks of higher pitch being less marked. When the vibration was made as strong as possible by means of bowing, the lowering of pitch was found to amount to a full semitone (15 : 16). Mr. Womack, Prof. Ramsay, and Dr. G. F. McCleary, who repeated the experiment, all agreed pretty nearly with my estimate: in each case the greatest apparent flattening observed was as much as a semitone.

With a large fork giving *c* (one octave lower) the effect was more striking. In this case the fork with its resonance-box was too unwieldy to be moved bodily to and fro, so it was allowed to stand on a table while the observer's head was lowered so as to bring one ear opposite to the opening of the resonance-box at a distance of a few inches. Thus the fork was heard with great intensity, while on raising the head through half a metre or so the loudness was greatly diminished. Here the lowering of pitch due to the greatest intensity of vibration which I could excite in the fork amounted usually to a minor third (5 : 6) or even more. Thus, repeating the experiment on different days, I have estimated the interval sometimes as rather more and sometimes as rather less than a minor third. Mr. Womack heard something between a minor and a major third; Professor Ramsay a full tone; Dr. McCleary more than a minor third.

4. Before saying more concerning the observations, it will be convenient to mention a physiological theory by which I have attempted to account for the observed effects. Helmholtz's discussion of the vibration of the basilar membrane in the cochlea is applicable only to infinitesimal amplitudes, inasmuch as all his equations of motion are linear, and though the introduction of terms of higher order would have made the investigation very lengthy and an exact solution impossible, it is not difficult to see on general grounds what

modification of the sense of pitch is to be expected from increased loudness. If the basilar membrane may be regarded as being stretched with a finite tension in the direction of its breadth, and as having no appreciable tension in the perpendicular direction, then Helmholtz shows that it will be vibrationally equivalent to a series of strings stretched side by side and unconnected with one another. For shortness, I shall speak of the membrane as if it actually consisted of such separate strings, and thus, following Helmholtz's theory, we are to suppose that a disturbance of given period reaching the ear excites the strongest resonance in those strings whose natural period is most nearly the same. Now when a string is vibrating freely with finite amplitude, the period of its vibrations is shorter than if the amplitude were infinitesimal; and we are accordingly led to enquire whether a periodic force of considerable intensity would not excite the maximum resonance in those strings whose natural period *for some finite vibration-amplitude* was most nearly the same.

5. As sufficiently representative of our case we may take a system with one degree of freedom, in which the positional force contains a term proportional to the cube of the displacement from equilibrium, as well as one proportional to the first power*, the equation of motion being accordingly written

$$F = m\ddot{x} + k\dot{x} + hx\left(1 + \frac{x^2}{a^2}\right), \quad . \quad . \quad . \quad . \quad (1)$$

where F is the external force impressed on the system, x is the displacement from the equilibrium position, and m, k, h, a are real constants.

If we take F to be a simple harmonic function of the time whose character has been maintained long enough for the whole motion to have become periodic, the value of x will be expansible in a Fourier's series in which the constant coefficients have to be determined. But the expressions thus obtained are very unwieldy; and it will therefore be more convenient to treat x instead of F as a simple harmonic function of the time. It is not easy to say definitely which assumption corresponds most nearly with the actual case, and from what follows I think it will be evident enough that whichever case we consider the general conclusions would be much the same.

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* Terms of even degree would imply that the free vibrations were not symmetrical with respect to the equilibrium position, and would therefore be absent in the case of a stretched string, which we have supposed to agree pretty nearly with the physiological case.

6. If we put, then, $x = \mathrm{B}\cos pt$,
the expression for the impressed force is

$$\mathrm{F} = -\mathrm{B}mp^2\cos pt - \mathrm{B}kp\sin pt + \mathrm{B}h\left(\cos pt + \frac{\mathrm{B}^2}{a^2}\cos^3 pt\right);$$

so that

$$\frac{\mathrm{F}}{\mathrm{B}} = \left\{-mp^2 + h\left(1 + \frac{3}{4}\frac{\mathrm{B}^2}{a^2}\right)\right\}\cos pt - kp\sin pt + \tfrac{1}{4}h\frac{\mathrm{B}^2}{a^2}\cos^3 pt.$$

Let F_1 denote the first harmonic term of F (that is, the sum of the terms in $\cos pt$ and $\sin pt$), while F_3 denotes the term in $\cos 3pt$. Then, since

$$\dot{x} = -\mathrm{B}p\sin pt,$$

we have

$$\frac{\mathrm{F}_1^2(\text{max.})}{\dot{x}^2(\text{max.})} = \frac{1}{p^2}\left\{-mp^2 + h\left(1 + \frac{3}{4}\frac{\mathrm{B}^2}{a^2}\right)\right\}^2 + k^2.$$

When m, k, h, a, and B are given, the minimum value of the right-hand side corresponds to

$$mp^2 = h\left(1 + \frac{3}{4}\frac{\mathrm{B}^2}{a^2}\right) > h.$$

Also

$$\frac{\mathrm{F}_3^2(\text{max.})}{\dot{x}^2(\text{max.})} = \frac{1}{16p^2}h^2\frac{\mathrm{B}^4}{a^4},$$

which diminishes continually as p^2 increases. Hence in general terms we may say that to produce a given amplitude of velocity requires the least amplitude of impressed periodic force when the periodic time of the force is *somewhat shorter* than would be the natural period of the system for infinitesimal vibrations if the frictional term were abolished. And returning to the case of our strings, we may infer that a similar result will hold good. Hence a force of given finite amplitude will excite in a given string the greatest amplitude of velocity when the period of the force is somewhat shorter than the "natural" period of the string, and hence when a periodic disturbance of finite amplitude reaches the ear, the string whose resonance is excited most strongly will have a "natural" period *longer* than the period of the disturbance.

7. For example, let the note *c* be sounded with very small intensity, and let that part of the basilar membrane which responds most strongly be called the *c*-string. If then the same note *c* is made to sound close to the ear with considerable intensity, the strongest resonance will be excited no longer in the *c*-string, but in some string of longer natural period, such as the B♭-string. Now according to Helmholtz's theory

of sound-perception our estimate of pitch depends entirely on localization of the most strongly agitated portion of the basilar membrane, so that in the case just considered, when the note *c* was made to change from a very small to a very much greater intensity, we should expect to hear not only an increase of loudness, but also a lowering of pitch.

8. At the same time it is not to be supposed that the agitation of the "*c*-string" is lessened when the intensity of the note *c* is augmented. The effect must necessarily be in the other direction, so that such a note powerfully sounded close to the ear must perceptibly excite a tract of the basilar membrane corresponding to a considerable *range* of pitch (the place of maximum disturbance being probably not far from the middle of this range).

9. We must even suppose that an increase in the intensity of a note without change of frequency causes the "range of stimulation" (as we may call it) to extend to patches *a little higher* than before, as well as to those a good deal lower.

10. In connexion with § 8 it may be remarked that, when the ear is kept close to the resonant cavity of a strongly-vibrating *c*-fork, the impression of pitch obtained is far from being very definite. One pitch or another within an appreciable range may be heard by a mere effort of attention. On the other hand, a more definite impression is obtained on alternating between smaller and greater intensities of the same note. Thus, on raising or lowering the head, as mentioned in § 3, the interval between the soft note and the loud note may appear at first to be about a minor third, when the fork is sounding strongly. As the amplitude of vibration dies down, the interval diminishes, and it is possible to say pretty definitely when it is just a whole tone, and when it is only a semitone; until, as the note in either position of the head becomes nearly inaudible, the apparent difference of pitch is obliterated.

11. If the orifice of the ear remote from the fork is left open, the sound reaching that ear will be less intense than is heard by the other ear, and the corresponding pitch will be higher. Though of course beats are entirely absent*, it might be thought that two distinct pitches would be heard simultaneously, but this requires a distinct effort of attention. The general impression is of a pitch intermediate between those which would be heard by the two ears separately, so that on

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* In the discussion Prof. S. P. Thompson suggested that, if the observations were valid, beats should occur between the notes heard by the two ears; but a consideration of the physical conditions will show that nothing of this kind is to be expected.

closing the further ear a distinct lowering of pitch takes place. For this reason the effects described in § 3 are most marked when the less stimulated ear is kept closed.

12. I have not yet mentioned an effect noticed by an observer in whom hearing with one ear was not normal. With the less sensitive ear the usual effect was reversed; that is, on bringing the ear close to the resonance-cavity of the *c*-fork, the pitch, instead of falling, appeared to rise by about a semitone. Even taking § 9 into account, this result seems rather anomalous.

13. Though variations of pitch accompanying variations of loudness must frequently have been observed, the physiological influences at work do not appear to have been suspected *. And yet these subjective influences must be by no means negligible in the case of wind-instrument players ; and even from players of stringed instruments I think I have heard that it is easier to judge of another player's intonation than to be quite certain about one's own. On the other hand, as regards the tuning of the intervals of consonant chords, it must be remembered that the actual criterion is usually the obliteration of beats, so that on this point the judgment is not disturbed by a small subjective uncertainty in the estimation of pitch. I have also convinced myself that, when harmonic upper partials are present, the sense of tonality is largely dependent upon them ; and harmonics from their higher pitch and generally feebler intensity will suffer less subjective repression of pitch than the fundamental.

II. *Objective Demonstration of Combination-Tones.*

14. When two notes differing in frequency are powerfully sounded in the neighbourhood of one another, secondary tones are produced, of which the most prominent have frequencies respectively equal to the sum and difference of the frequencies of the parent tones. It has been maintained by some writers that these secondary tones are purely subjective, and have no existence external to the ear, and the following experiment was designed to show that in some cases at least the first difference-tone has a real physical existence. If the vibration of the air external to the ear has really a component of the frequency in question, we must suppose this component to have arisen from a failure of the principle of superposition, that is, from the circumstance that as the parent vibrations

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* For example, Lord Rayleigh mentions ('Theory of Sound,' 2nd ed. vol. i. § 67) that "tuning-forks rise a little, though very little, in pitch as the vibration dies away."

are of considerable amplitude, the equations of motion cannot be regarded as sensibly linear; and accordingly it is to be expected that if two sources of sound are brought closer together, the intensity of the difference-tone will increase. I have used two stopped organ-pipes of white metal giving the notes *e'* and *g'*, the difference-tone being consequently C. The pipes are connected to a well-weighted organ-bellows by flexible rubber tubes, and the distance between them can be varied at will from a few feet to a couple of inches (the walls of the two pipes being then in contact). It is best for the listener to be stationed in a distant room, so that the sound which reaches him is only of moderate intensity, while the comparatively small distances through which the pipes are moved does not appreciably affect the sounds which they individually send to his ear. The bellows being filled, the sounding pipes are held alternately far apart and near together, and each time, as they nearly approach one another, the difference-tone C_1 is heard to boom out with greatly increased intensity. From this, I would suggest, we are to infer that the difference-tone has a real objective existence.

(Further experiments have *not* confirmed this result. Even Prof. Rücker's very sensitive arrangement of interference-bands failed to show any objective difference-tone from the two organ-pipes, suitably tuned. An attempt will be made to deal with the subject more fully in a subsequent paper.)

XLIV. *Glacier-Grains.*

To the Editors of the Philosophical Magazine.

10 Charnwood Street, Derby,
April 3, 1895.

GENTLEMEN,

IN 1888 I communicated to the February No. of the Phil. Mag. a short paper on glacier motion. Since then I have had an opportunity of examining, in company with Mr. G. Fletcher, F.G.S., the structure of some of the largest Swiss and Norwegian glaciers. The results of our investigation are given in a paper printed in the April number of the Geological Magazine for the current year.

In it we show that the small granular particles of ice resulting from the partial melting and refreezing of the snow, and also the minute crystal particles collected during frosty sunless days, in course of time, when they have become welded by pressure into a compact mass, undergo a striking change. The greater number of the granules and crystalline particles disappear, the molecules composing them going to build up a comparatively small number of large crystalline particles. In our paper we remark*: "Although it is not quite clear why some of the grains should increase in size and others disappear, the transference of the molecules from crystal to crystal offers no difficulty. . . . ."

Since this was written I have been led to think that the known laws regulating surface-tension phenomena perhaps afford an explanation for the disappearance of the smaller granules and the growth of the larger ones.

Glacier-ice consists of a kind of conglomerate formed of glacier-grains. These grains have very irregular outlines and fit closely together. Figs. 1 and 2 are drawings of slices of glacier-ice as seen under polarized light.

Fig. 1.

($\frac{1}{1}$) Horizontal slice from the Eismeer of Untergrindelwald Glacier.

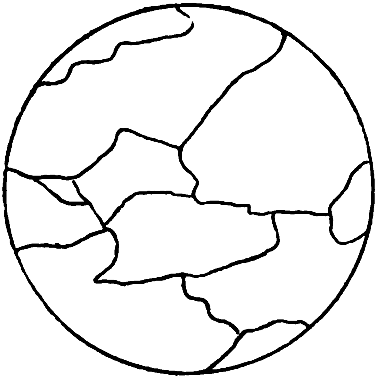

Fig. 2.

($\frac{1}{1}$) Vertical section from Mer de Glace Glacier.

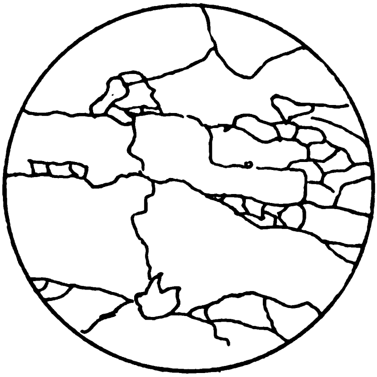

Fig. 2 is a sample of veined ice, the crystalline particles having been sheared by the motion of the glacier.

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* Geol. Mag. April 1895, p. 155.

Between each grain and its neighbours there is a true *surface*, the *tension* of which probably depends in some measure upon the relationship of their axes to each other.

Now we know that a by no means unimportant portion of the energy of a solid body depends upon its surface area; and I would suggest also that it depends in some measure upon the surfaces separating the crystal units, of which it is composed, from each other, even when they are of similar composition.

In a block of glacier-ice, therefore, or in a block of granite, the total energy depends, not only upon its temperature and volume, but also upon the energy of the surface-tensions of its component grains, whether they be similar or dissimilar in composition.

Now it is an important theorem of Dynamics that, for the stable equilibrium of a system, the potential energy of the whole must be a minimum. For instance, when immiscible liquids are intimately mixed, work is done in increasing their surface-energy, and the energy thus rendered potential serves to again separate them. Glacier-ice is in much the same condition. Its potential energy is always tending to a minimum, a condition which can only be reached by the disappearance of the interfaces between the crystal-grains. Being viscous, it is unable to do more than delay the disappearance of the interfaces, and the grains would continue to grow larger and larger with the lapse of time were it not for the fact that they are broken in the production of the ribboned or veined structure.

For the same reason masses of all liquids possessing structure, whatever their viscosities may be, eventually become single crystalline particles.

Yours truly,
R. M. Deeley.

XLV. *On the Kinetic Interpretation of the Dissipation Function.* *By* Dr. Ladislas Natanson, *Professor of Natural Philosophy, University of Cracow*[*].

1. In the following paper we consider a fluid medium from Maxwell's point of view (see the paper "On the Dynamical Theory of Gases," 'Scientific Papers,' ii. 26); we suppose it to be composed of a great number of moving molecules. Let ξ, η, ζ be the components of the individual (or "molecular") velocity of a molecule; and let u, v, w be

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[*] Translated from "*Rozprawy*" (Transactions) of the Cracow Academy of Sciences, Math. and Phys. Section, vol. xxix. Communicated by the Author.

the components of the mean (or "molar") velocity within an element $dx\,dy\,dz$ of volume; $n\,dx\,dy\,dz$ may represent the number of molecules within that element. The mass of a molecule being M, $\rho=Mn$ being the density of the medium, the kinetic energy of a molecule is

$$\tfrac{1}{2}M\{(u+\xi)^2+(v+\eta)^2+(w+\zeta)^2\}; \quad . \quad . \quad . \quad (1)$$

and the total kinetic energy of a portion of the medium consists of the two following parts:—(1) the kinetic energy of the visible motion,

$$K=\tfrac{1}{2}\iiint\rho(u^2+v^2+w^2)\,dx\,dy\,dz; \quad . \quad . \quad . \quad (2)$$

it is this energy that, in Hydrodynamics, is taken into account; (2) the molecular or heat-energy,

$$E=\tfrac{1}{2}\iiint\rho(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\,dx\,dy\,dz. \quad . \quad . \quad . \quad (3)$$

In these expressions the integrations are supposed to be performed throughout the volume occupied by the medium; and $\overline{\xi^2}$ and similar symbols represent the mean values of ξ^2 &c. for the molecules within an element. We have

$$\overline{\xi}=0; \quad \overline{\eta}=0; \quad \overline{\zeta}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

At the point (x, y, z) we have the normal component pressures,

$$p_{xx}=\rho\overline{\xi^2}; \quad p_{yy}=\rho\overline{\eta^2}; \quad p_{zz}=\rho\overline{\zeta^2}; \quad . \quad . \quad . \quad (5)$$

and the tangential,

$$p_{yz}=p_{zy}=\rho\overline{\eta\zeta}; \quad p_{zx}=p_{xz}=\rho\overline{\zeta\xi}; \quad p_{xy}=p_{yx}=\rho\overline{\xi\eta}. \quad . \quad (6)$$

Let Q be any property of the molecule which can be expressed as a function of $(u+\xi)$, $(v+\eta)$, and $(w+\zeta)$. Then writing d/dt for the actual or total variation of $\overline{Q}$, and $\delta/\delta t$ for any alteration of $\overline{Q}$ that can be due to the mutual interference of molecules,

$$\rho\frac{d\overline{Q}}{dt}+\frac{\partial}{\partial x}(\overline{\xi Q}\rho)+\frac{\partial}{\partial y}(\overline{\eta Q}\rho)+\frac{\partial}{\partial z}(\overline{\zeta Q}\rho)$$
$$=\rho\frac{\delta\overline{Q}}{\delta t}+\rho X\frac{\partial\overline{Q}}{\partial u}+\rho Y\frac{\partial\overline{Q}}{\partial v}+\rho Z\frac{\partial\overline{Q}}{\partial w}; \quad . \quad (7)$$

X, Y, Z denote here the components, at (x, y, z), of acceleration due to external forces. From this fundamental equation (7) the equation of continuity, as well as the equations of motion,

$$\rho\frac{du}{dt}+\frac{\partial}{\partial x}(\rho\overline{\xi^2})+\frac{\partial}{\partial y}(\rho\overline{\eta\xi})+\frac{\partial}{\partial z}(\rho\overline{\zeta\xi})=\rho X, \quad . \quad . \quad (8)$$

immediately follow. Let us now put

$$Q=(u+\xi)^2+(v+\eta)^2+(w+\zeta)^2; \quad . \quad . \quad . \quad . \quad (9)$$

we obtain

$$\begin{aligned}
&\rho\frac{d}{dt}(u^2+v^2+w^2+\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\\
&\quad+\frac{\partial}{\partial x}(2u\rho\overline{\xi^2}+2v\rho\overline{\xi\eta}+2w\rho\overline{\xi\zeta}+\rho\overline{\xi^3}+\rho\overline{\xi\eta^2}+\rho\overline{\xi\zeta^2})\\
&\quad+\frac{\partial}{\partial y}(2u\rho\overline{\eta\xi}+2v\rho\overline{\eta^2}+2w\rho\overline{\eta\zeta}+\rho\overline{\eta\xi^2}+\rho\overline{\eta^3}+\rho\overline{\eta\zeta^2})\\
&\quad+\frac{\partial}{\partial z}(2u\rho\overline{\zeta\xi}+2v\rho\overline{\zeta\eta}+2w\rho\overline{\zeta^2}+\rho\overline{\zeta\xi^2}+\rho\overline{\zeta\eta^2}+\rho\overline{\zeta^3})\\
&\quad=2\rho(uX+vY+wZ)+\rho\frac{\delta}{\delta t}(u^2+v^2+w^2+\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2}). \quad (10)
\end{aligned}$$

By (8) this equation is reduced to

$$\begin{aligned}
&\tfrac{1}{2}\rho\frac{d}{dt}(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})+\rho\overline{\xi^2}\frac{\partial u}{\partial x}+\rho\overline{\eta^2}\frac{\partial v}{\partial y}+\rho\overline{\zeta^2}\frac{\partial w}{\partial z}\\
&\quad+\rho\overline{\eta\zeta}\left(\frac{\partial v}{\partial z}+\frac{\partial w}{\partial y}\right)+\rho\overline{\zeta\xi}\left(\frac{\partial w}{\partial x}+\frac{\partial u}{\partial z}\right)+\rho\overline{\xi\eta}\left(\frac{\partial u}{\partial y}+\frac{\partial v}{\partial x}\right)\\
&\quad+\tfrac{1}{2}\frac{\partial}{\partial x}(\rho\overline{\xi^3}+\rho\overline{\xi\eta^2}+\rho\overline{\xi\zeta^2})+\tfrac{1}{2}\frac{\partial}{\partial y}(\rho\overline{\eta\xi^2}+\rho\overline{\eta^3}+\rho\overline{\eta\zeta^2})\\
&\quad+\tfrac{1}{2}\frac{\partial}{\partial z}(\rho\overline{\zeta\xi^2}+\rho\overline{\zeta\eta^2}+\rho\overline{\zeta^3})\\
&\quad=\tfrac{1}{2}\rho\frac{\delta}{\delta t}(u^2+v^2+w^2+\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2}). \quad \ldots\ldots\ldots \quad (11)
\end{aligned}$$

All these equations are quite independent of any view we may entertain as to the intimate nature of molecules and as to the law of force between them ; accordingly they may be said to belong to the *Kinematical* Part of the Theory of constitution of fluids.

2. If we suppose that the molecules of the fluid do not contain any internal energy (or that they contain such energy in absolutely constant amount) the energy of a molecule will be only that which depends on the velocity of its centre of inertia. Assuming this equation (11) may be transformed. Put for brevity,

$$\frac{\partial u}{\partial x}=a\,;\quad \frac{\partial v}{\partial y}=b\,;\quad \frac{\partial w}{\partial z}=c\,;\quad \ldots\ldots \quad (12)$$

$$\frac{\partial v}{\partial z}+\frac{\partial w}{\partial y}=A\,;\quad \frac{\partial w}{\partial x}+\frac{\partial u}{\partial z}=B\,;\quad \frac{\partial u}{\partial y}+\frac{\partial v}{\partial x}=C\,;\ . \ (13$$

and let us add to the left-hand side

$$\tfrac{1}{2}(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\frac{d\rho}{dt}+\tfrac{1}{2}\rho(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\theta, \quad \ldots \quad (14)$$

where $\theta=a+b+c$. Multiplying by $dx\,dy\,dz$ and integrating throughout the volume occupied by the medium, we have then

$$\frac{\partial E}{\partial t}+\tfrac{1}{2}\iint\rho(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})(lu+mv+nw)\,dS$$

$$+\iiint[\rho\overline{\xi^2}a+\rho\overline{\eta^2}b+\rho\overline{\zeta^2}c+\rho\overline{\eta\zeta}A+\rho\overline{\zeta\xi}B+\rho\overline{\xi\eta}\,C]\,dx\,dy\,dz=0\,; \quad (15)$$

here the direction-cosines of the normal to the element dS of the surface are denoted by l, m, n. If the medium cannot flow across the surface, the second term on the left-hand side may be omitted. Assuming this and calculating $\partial K/\partial t$ from equations (8) in a similar way we find

$$\frac{\partial K}{\partial t}-\iiint[\rho\overline{\xi^2}a+\rho\overline{\eta^2}b+\rho\overline{\zeta^2}c+\rho\overline{\eta\zeta}A+\rho\overline{\zeta\xi}B+\rho\overline{\xi\eta}C]\,dx\,dy\,dz$$

$$=\iiint\rho(uX+vY+wZ)\,dx\,dy\,dx\,; \quad .\ .\ (16)$$

hence

$$\frac{\partial K}{\partial t}=-\frac{\partial E}{\partial t}+\iiint\rho(uX+vY+wZ)\,dx\,dy\,dz, \quad .\ .\ (17)$$

i.e. molar energy is subject to change from two sources, the first being the influence of external forces, the second being the possible transformation of molecular energy E into molar energy K or *vice versâ*. Let us denote the rate of change of K due to the second source of variation by $\partial' K/\partial t$; we have

$$\frac{\partial E}{\partial t}=-\frac{\partial' K}{\partial t}=-\iiint[\rho\overline{\xi^2}a+\rho\overline{\eta^2}b+\rho\overline{\zeta^2}c+\rho\overline{\eta\zeta}A+\rho\overline{\zeta\xi}B+\rho\overline{\xi\eta}C]\,dx\,dy\,dz. (18)$$

Let us put

$$3p=\rho\overline{\xi^2}+\rho\overline{\eta^2}+\rho\overline{\zeta^2}. \quad .\ .\ .\ .\ .\ .\ .\ (19)$$

$$\left.\begin{aligned}F&=(p-\rho\overline{\xi^2})a+(p-\rho\overline{\eta^2})b+(p-\rho\overline{\zeta^2})c-\rho\overline{\eta\zeta}A-\rho\overline{\zeta\xi}B-\rho\overline{\xi\eta}C\\&=-\rho\overline{\xi^2}(a-\tfrac{1}{3}\theta)-\rho\overline{\eta^2}(b-\tfrac{1}{3}\theta)-\rho\overline{\zeta^2}(c-\tfrac{1}{3}\theta)-\rho\overline{\eta\zeta}A-\rho\overline{\zeta\xi}B-\rho\overline{\xi\eta}C\\&=(p-\rho\overline{\xi^2})(a-\tfrac{1}{3}\theta)+(p-\rho\overline{\eta^2})(b-\tfrac{1}{3}\theta)+(p-\rho\overline{\zeta^2})(c-\tfrac{1}{3}\theta)\\&\qquad-\rho\overline{\eta\zeta}A-\rho\overline{\zeta\xi}B-\rho\overline{\xi\eta}C.\end{aligned}\right\}\ (20)$$

Equation (18) may then be written

$$\frac{\partial E}{\partial t}=-\frac{\partial' K}{\partial t}=\iiint(F-p\theta)\,dx\,dy\,dz\,; \quad .\ .\ .\ (21)$$

the molecular energy E is therefore subject to change from two sources: first, the work of the ordinary average pressure, and second, the effect of a disturbance giving rise to tangential pressures and to inequality of the normal ones, F being the rate (per unit of volume and time) at which molecular energy is generated by the effect of the disturbance.

Put in (7)

$$Q=(u+\xi)^2\,; \quad Q=(v+\eta)(w+\zeta)\,; \quad .\ .\ (22)$$

if the disturbance is not very violent, we shall find

$$\frac{\delta}{\delta t}(p-\rho\overline{\xi^2})=-2p(a-\tfrac{1}{3}\theta). \quad . \quad . \quad . \quad . \quad (23)$$

$$\frac{\delta}{\delta t}(\rho\overline{\eta\zeta})=p\mathrm{A}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

and other equations which may be written down from symmetry. Hence

$$\mathrm{F}=-\frac{1}{4p}\frac{\delta}{\delta t}\{(p-\rho\overline{\xi^2})^2+(p-\rho\overline{\eta^2})^2+(p-\rho\overline{\zeta^2})^2$$
$$+2(\rho\overline{\eta\zeta})^2+2(\rho\overline{\zeta\xi})^2+2(\rho\overline{\xi\eta})^2\}. \quad . \quad (25)$$

From this it appears that the direction of that transformation of energy the rate of which is F depends on the nature of the mutual action between molecules. Molar energy will become converted into molecular energy if molecular interaction is such as to tend to diminish the absolute values of the terms $p-\rho\overline{\xi^2}$, $\rho\overline{\eta\zeta}$ and similar terms; *i. e.* such as to tend gradually to calm the disturbance existing: F is then always a positive quantity and the opposite transformation of molecular energy into molar energy is impossible. That this is precisely what is realised in all fluids in Nature, as attested by the phenomenon of viscosity, cannot, however, be deduced from Kinematical Theory. We have ascertained, as it were, the path of change of the molar energy, but we are unable to say why one of the two possible directions of change is always selected.

If now we suppose the following equations to be given:—

$$p-\rho\overline{\xi^2}=2\mu(a-\tfrac{1}{3}\theta), \quad . \quad . \quad . \quad . \quad . \quad (26)$$

$$\rho\overline{\eta\zeta}=-\mu\mathrm{A}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

(the symbol μ denoting a constant, the coefficient of viscosity), and four other equations, to be written down from symmetry, we shall find it possible to complete our solution. Maxwell deduced these equations from his well-known assumption as to the law of force between molecules; Poisson, Sir G. G. Stokes, and others have given them in the ordinary Theory of Viscosity. It follows, then, that

$$\left.\begin{aligned}\mathrm{F}&=\frac{1}{\mu}\{\tfrac{1}{2}(p-\rho\overline{\xi^2})^2+\tfrac{1}{2}(p-\rho\overline{\eta^2})^2+\tfrac{1}{2}(p-\rho\overline{\zeta^2})^2+(\rho\overline{\eta\zeta})^2+(\rho\overline{\zeta\xi})^2+(\rho\overline{\xi\eta})^2\},\\ &=\mu\{2(a-\tfrac{1}{3}\theta)^2+2(b-\tfrac{1}{3}\theta)^2+2(c-\tfrac{1}{3}\theta)^2+\mathrm{A}^2+\mathrm{B}^2+\mathrm{C}^2\}\\ &=\frac{1}{\mu}\{\tfrac{1}{6}(\rho\overline{\eta^2}-\rho\overline{\zeta^2})^2+\tfrac{1}{6}(\rho\overline{\zeta^2}-\rho\overline{\xi^2})^2+\tfrac{1}{6}(\rho\overline{\xi^2}-\rho\overline{\eta^2})^2+(\rho\overline{\eta\zeta})^2+(\rho\overline{\zeta\xi})^2+(\rho\overline{\xi\eta})^2\}\\ &=\mu\{\tfrac{2}{3}(b-c)^2+\tfrac{2}{3}(c-a)^2+\tfrac{2}{3}(a-b)^2+\mathrm{A}^2+\mathrm{B}^2+\mathrm{C}^2\},\end{aligned}\right\} \quad (28)$$

and thus F can never assume negative values. Also

$$F=\mu(2a^2+2b^2+2c^2-\tfrac{2}{3}\theta^2+A^2+B^2+C^2), \quad . \quad . \quad (29)$$

this is the expression for the "Dissipation Function" F originally given by Lord Rayleigh. The cause for this denomination is obvious. Suppose a, b, c, A, B, C to have their sign changed; the sign of $p\theta$ will change but that of F will not; hence the term $p\theta$ corresponds to a reversible, the term F to an irreversible phenomenon. Indeed the conversion of molar energy into molecular energy which goes on, of whatever kind the existing disturbance may be, is irreversible. We have thus before us an example of Dissipation of Energy in a purely dynamical system.

3. If we now suppose that every molecule possesses an amount Mh of internal energy in addition to that which depends on its motion of translation, we shall have

$$\frac{\delta}{\delta t}\left[\tfrac{1}{2}\rho(u^2+v^2+w^2+\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})+\rho\bar{h}\right]=0. \quad . \quad (30)$$

Now it is easily seen that $\delta\bar{h}/\delta t$ and $d\bar{h}/dt$ are equivalent, since $\bar{h}$ cannot be affected by external forces any more than by convection; therefore

$$\tfrac{1}{2}\rho\frac{d}{dt}(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2}+\rho\frac{d\bar{h}}{dt}+\rho\overline{\xi^2}a+\rho\overline{\eta^2}b+\rho\overline{\zeta^2}c+\rho\overline{\eta\zeta}A+\rho\overline{\zeta\xi}B+\rho\overline{\xi\eta}C$$

$$+\tfrac{1}{2}\frac{\partial}{\partial x}(\rho\overline{\xi^3}+\rho\overline{\xi\eta^2}+\rho\overline{\xi\zeta^2})+\tfrac{1}{2}\frac{\partial}{\partial y}(\rho\overline{\eta\xi^2}+\rho\overline{\eta^3}+\rho\overline{\eta\zeta^2})$$

$$+\tfrac{1}{2}\frac{\partial}{\partial z}(\rho\overline{\zeta\xi^2}+\rho\overline{\zeta\eta^2}+\rho\overline{\zeta^3})=0. \quad . \quad . \quad . \quad . \quad . \quad (31)$$

Maxwell puts $\rho\bar{h}=\tfrac{1}{2}(\beta-1)\rho(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})$; if this relation is adopted, equation (31) will be that numbered (94) in Maxwell's paper, with a difference of factor, however, in the terms relating to conduction of heat. The foregoing deduction will not be subject to the criticism which M. Poincaré has offered with respect to Maxwell's deduction (see *Comptes Rendus*, vol. cxvi. p. 1017; see also *ibidem*, p. 1165, where the internal energy of the molecules is taken into account in the same way as that here adopted).

XLVI. *Experiments on the Radiation of Heated Gases.* *By* John Evershed*.

[Plate VII.]

THE renewed interest aroused in certain fundamental questions in spectroscopy by the publication of the researches of Pringsheim, Paschen, and Smithells has led me recently to undertake a series of observations on the visible radiations of certain elementary substances, particularly iodine and sodium, when their vapours are subjected to external heating. The important article published in the Philosophical Magazine (March 1894), by Prof. Smithells, may be said to have furnished the main incentive in this work, as it likewise determined the direction followed in the experiments.

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* Communicated by the Author.

I am further indebted to Prof. Smithells, to whom I submitted a statement of my results, for valuable advice and criticism, which has enabled me to anticipate certain objections that might have been raised to my conclusions.

The experiments were undertaken primarily with a view to obtaining a closer personal acquaintance with what I may call the "spectroscopic behaviour" of heated gases. I had no idea that they would lead to results which could throw any new light on the questions discussed in Prof. Smithells paper. Nevertheless, after continuing the experiments in a somewhat desultory fashion for some six months, and with very simple appliances, certain facts have presented themselves in a prominent way, which, so far as I can discover, have not been sufficiently noticed by previous workers, and which would appear to lend a strong support to the view there advocated, namely, that the luminosity of gases in flames may be directly due to high temperature, and that external heating is in itself sufficient to make a gas emit visible rays.

The fact that iodine vapour can be easily made incandescent by external heating was noticed by Salet (*Spectroscopie*, p. 173); and in the article above mentioned Prof. Smithells concludes that this luminosity can only be due to heat, and that chemical action plays no part in the phenomenon. It seemed, therefore, of interest to determine, first, the character of this iodine emission, and then to discover whether the property of glowing by mere heating was peculiar to iodine, or was shared in greater or less degree by other allied elements when vaporized, particularly by those which exhibit strong absorptive properties on light. After having thus gained some experience with the less easily oxidizable metalloids, I proposed finally to approach the question of the radiation of heated metallic vapours, to determine whether or not their characteristic spectra can be produced by mere heating.

It will perhaps be worth while at the outset to describe briefly a few simple experiments made to determine whether the iodine glow is affected in any way by the nature of the gas in which it is heated. I will describe them as nearly as possible in the order in which they were performed.

Experiment I.—A little iodine was placed near the closed end of a piece of hard glass tube of about 7 mm. bore, the other end being open to the atmosphere. This was suspended horizontally, and a Bunsen flame brought under the central part; when about 5 or 6 cm. of the tube had become nearly red-hot, the flame was held for a few seconds under the part containing the iodine, which immediately volatilized, filling the whole tube with coloured vapour. A bright reddish glow then appeared in the heated portion of the tube.

Exp. II.—Iodine was heated in a tube as in I. but closed to the atmosphere, and in which air was replaced by nitrogen. No difference was seen in the emission of light.

Exp. III.—The same as II., excepting that hydrogen was substituted for nitrogen. In this case also the glowing appeared, the same as before, but it could not be maintained as combination took place between the hydrogen and iodine, and the colourless hydriodic acid formed emitted no light.

Exp. IV.—In CO_2 the same result was obtained as in nitrogen.

Exp. V.—A thick glass tube containing iodine was exhausted with an air-pump until the pressure fell to about 20 mm. It was then heated so as to expel the remaining air by volatilizing a portion of the iodine, and then sealed off. The whole length of the exhausted tube was next warmed up until the density of the iodine vapour was sufficient to give the usual deep violet colour. On strongly heating a short section of the tube at this stage, the usual reddish-yellow glow appeared exactly as in the other experiments.

These preliminary experiments, therefore, as far as they go, entirely favour the view that the glowing is determined by heat alone, and not by chemical "luminescence." For the phenomenon appears to be quite independent of the gas in which the iodine is heated, and in III., where chemical combination actually occurs, the light, instead of being intensified, is extinguished.

To determine the character of the light, things were arranged as in I., the glowing tube being observed with a spectroscope, having a lens in front to throw an image of the hot part of the tube across the slit of the instrument. Before heating the iodine a faint streaky spectrum, due to glowing opaque particles in the glass, was all that could be seen; but immediately the iodine was vaporized a bright spectrum shone out. This appeared perfectly continuous, and similar to that given by a red-hot iron wire, with which it was directly compared. No sign of resolution into lines could be made out even with a highly dispersive train of five prisms.

Next a ray of white light from the flame of a paraffin lamp was made to pass through the glowing tube and enter the spectroscope, after having suffered absorption by the heated vapour.

The dark bands, characteristic of cooler iodine vapour, were seen to be unchanged, and there was no sign of any continuous absorption. Thus at the temperature of the experiment iodine emits a continuous spectrum, and does not emit only those rays which it absorbs.

The question whether iodine is the only element having this property of glowing with a continuous spectrum at comparatively low temperatures was next investigated. A series of experiments with the allied element bromine immediately showed that this was not so, for the vapour of this substance was also found to glow brightly under similar circumstances. The bromine glow seems indeed to be quite as conspicuous as that of iodine: the spectrum also was found to be perfectly continuous.

It was then thought that chlorine, being also a coloured gas and allied to the others, would probably be found to emit light in the same way. Accordingly arrangements were made for generating and thoroughly drying this gas and heating it in a glass tube, as in the foregoing experiments. The first attempts to see the glow were made, as before, from outside the tube; but they led to negative, or, at the most, very doubtful results. A very slight alteration in the mode of viewing the heated gas soon, however, revealed a distinct and unmistakable, though faint, luminosity. The experiment was arranged in the following way:—Chlorine from a generating flask, after being freed from HCl and dried by passing slowly through a long tube of calcium chloride, was led into a straight piece of combustion-tube of about 7 mm. bore, heated strongly in the middle. This tube connected on to a larger glass tube containing a total-reflexion prism placed in line with the central axis of the heated tube: this enabled one to observe the heated gas "end on" without the interposition of the red-hot glass, and a dark background was obtained by covering up the further end of the combustion-tube with opaque material.

In this way observations were made, first, with common air only passed through the apparatus, and afterwards with dried chlorine, about 5 cm. of the tube being kept meanwhile at the highest temperature attainable with an ordinary Bunsen burner. With air, the centre of the tube remained perfectly dark, and no trace of glowing solid matter in the form of dust could be seen. With chlorine, on the other hand, a faint greenish glow gradually filled up the previously dark central bore of the tube, appearing first on the lower or hottest part. The light, although brighter on the lower side, appeared perfectly uniform in texture so to speak, unlike the glow produced by incandescent solid particles, which can be seen under certain circumstances as wreaths and streaky clouds moving with the convection-currents in the tube *.

Being satisfied by repeated trials that the glow was really due to incandescent chlorine, an endeavour was made to determine the spectroscopic character of the light. It seemed almost hopeless to observe the spectrum directly, although with a spectroscope of very low dispersion and wide slit the spectrum appeared to be continuous; but it could only be traced between the positions of D and F of the solar spectrum, probably owing to the greater sensitiveness of the eye to that region. An indirect method was, however, devised. The depth of the layer of cool chlorine traversed by the light from the hot gas was, in the first instance, about 20 cm., that being the distance between the prism and the hot part of the tube. The absorbing effect of this thickness of gas was tested by varying the distance, heating the tube successively at 15 and 30 cm. from the prism. If the spectrum of the light emitted consisted of lines or bands corresponding to the absorption-lines of chlorine, there should be a marked increase of absorption after traversing 30 cm. as compared with 15 cm. But no difference was perceptible in the intensity of the glow whatever the distance traversed, showing that the cool gas exercises very little absorption on the light coming from the hot.

The inference, therefore, is that chlorine, like iodine and bromine, emits other rays than those absorbed, and probably shines with continuous light; the selective absorption of the cool gas merely giving the glow a greenish tint.

There seems no reason to doubt that the luminosity of chlorine, as of its allied elements, is directly due to the heating, and that chemical changes are not concerned in the phenomenon.

The Sulphur Group.—Similar results have been obtained with sulphur and selenium. The glowing may be observed either "end on" in a red-hot porcelain tube filled with hydrogen or nitrogen, or the element may be simply sealed in a hard glass tube in air. If a small portion of the tube be then heated strongly, a faint glow can be seen while distillation is going on, and the heated space is filled with vapour.

Phosphorus.—Experiments with this substance have so far led to negative results. After all the phosphorescence due to traces of oxygen has disappeared from the tube, the vapour appears to give no light.

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* The glowing of heated chlorine may be more conveniently observed in a porcelain tube connected with a T-tube having a glass plate cemented in one end of the T. If the Bunsen is concentrated on the tube by means of a fire-clay arch placed over it, the glow uniformly illuminates the bore of the tube.

Arsenic.—The vapour of this substance glows distinctly when heated in nitrogen. In hydrogen also the glow is distinct, but fainter than in nitrogen.

To sum up, then, it appears that besides iodine, the vapours of bromine, chlorine, sulphur, selenium, and arsenic can all be made more or less incandescent by heating to the temperature at which glass combustion-tube softens, and the light emitted by each of these glowing vapours appears to give a perfectly continuous spectrum; whilst the corresponding absorption spectra are selective. Thus there is no such close relation between emission and absorption as is implied by Kirchhoff's law of radiating bodies. There seems, however, to be a general relation between the total absorbing and radiating power for the visible rays: those vapours which are highly coloured and absorb strongly in the visible spectrum also radiate conspicuously in that part of the spectrum, whilst colourless non-absorbing vapours, such as phosphorus, emit no perceptible light when heated.

That the glowing in these cases in no way differs from the glowing of heated solids seems, to say the least, extremely probable, for there is no evidence whatever that chemical changes accompany the luminosity; and there is besides the fact that when direct combination does occur between the vapour and the gas in which it is heated, as in the case of iodine in hydrogen, and possibly also arsenic in hydrogen, there is no luminous effect at all.

It may be questioned, however, whether molecular dissociation may not be concerned in the radiation, or alternate dissociation and reaggregation of the atoms of the molecules. For, according to the kinetic theory, at a given temperature and pressure the vapours may contain a certain proportion of free atoms distributed among the more complex molecular groups, but the individuality of these uncombined atoms will continually change whilst the proportion remains the same, for there will be a constant reaction or interchange going on between the atoms and the molecules. The emission of light may be supposed to depend on this act of union or disunion of the atoms, the radiant energy being indirectly derived from the heat supplied to the system to maintain the temperature.

Thus in the case of the diatomic gases iodine, bromine, and chlorine, a proportion of the molecules I_2, Br_2, Cl_2 may dissociate into 2I, 2Br, 2Cl, and sulphur vapour may similarly dissociate from S_6 to $3S_2$, and so on. From recent determinations of the vapour densities of the halogens, it appears that iodine begins to dissociate between 600° and 700° C., at a pressure of 1 atmosphere*. Chlorine, on the other hand, remains at a normal density corresponding to Cl_2 between about 200° and 1200° C. * With regard to the former element, the temperature at which dissociation commences (say 600°) is not much above that at which the glowing is first seen, and as in most of the experiments the iodine or bromine vapour is largely diluted with a neutral gas, so that the partial pressure is a good deal less than one atmosphere, it might well be supposed that dissociation was going on even at the lowest temperature at which the glow can be seen. But in the case of chlorine dissociation begins at some 500° above the temperature of my experiments (assumed at about 700°) : moreover, there is no dilution of gas, which is observed at the atmospheric pressure, so there can be no question of dissociation here ; or at any rate, as there is no independent evidence of it, we have no more right to assume it as a cause of the luminosity than we have in the case of glowing solids.

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* Crafts and Meier, *Ber. deut. chem. Ges.* xiii.

But, apart from the fact that chlorine can be made incandescent although it is not dissociating, it appears to me that the general relation mentioned above between radiation and absorption of the visible rays, and the fact that the intensity of the glowing of the more absorptive vapours (the others being too difficult to observe) appears to closely follow that of a solid raised simultaneously through the same range of temperature †, gives strong support to the view that there is no essential difference between gases and solids in the manner in which they radiate, at any rate under the conditions of the foregoing experiments. If dissociation were concerned, say, in the case of glowing iodine, one would expect the intensity of the light to rapidly increase when the temperature is made to approach the actual temperature of dissociation, where the maximum interaction of the atoms occurs. It should in fact increase in a much greater ratio than in the case of a glowing solid. But I have failed to detect any evidence of such relative increase on the part of either iodine or any other glowing gas. Further, a decrease of density (by exhaustion or dilution) will facilitate dissociation, and thus should tend to counteract the reduction of luminosity due to a smaller number of molecules concerned. But no such effect is in fact to be seen under these conditions.

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* J. M. Crafts, *ibid.* xvi.; also Jahn, *ibid.* xv.

† The radiation from iodine may be easily compared with that of a solid at the same temperature, by placing a small piece of carbon inside the heated portion of the glass tube described in exp. I. Also when the glass contains opaque particles, these are seen to glow with the same intensity as the iodine, whatever the temperature, when the vapour is of sufficient density to give the maximum luminosity.

The Sodium Radiation.

Having thus far failed to produce discontinuous spectra by external heating, I next tried what could be done with metallic vapours. Sodium was the metal chosen for the initial experiments, the powerful absorption produced by the vapour of this element on "D" light seeming, on Kirchhoff's hypothesis, to give the best chance of success at the very moderate temperatures I could command with a single large Bunsen flame.

The form of apparatus used in the earlier experiments was designed with a view to excluding, as far as possible, from the tube in which the sodium was to be heated any gaseous substances that might be expected to react chemically with the vapour of the metal: the emission phenomena produced under these conditions being then compared with that produced when traces of oxygen or moisture were purposely allowed to remain in the neutral gas in which the sodium was volatilized. In the diagram (Plate VII. fig. 1) A and B are two similar gas-holders; a rubber tube leads from A to a couple of wash-bottles S′, S″, containing strong sulphuric acid; from S″ a long tube of hard glass, P, containing a little phosphorus leads into the drying-tube C, which is packed with calcium oxide and calcium chloride—the former to remove carbonic acid, and the latter traces of water which may remain in the gas used after passing the sulphuric-acid bottles. The drying-tube connects on to the porcelain heating-tube H through a metal T-piece, one end of the T having a glass plate carefully cemented in so that one may look along the inside of the heating-tube, to which the T is connected by rubber tube tightened with wire, both connexions being also buried in sealing-wax. At the other end of H, which is covered in the centre by a fireclay arch, is a second T of glass, one limb connecting with a glass gland or stuffing-box, G, with pierced rubber ends, and filled with mercury. A long steel rod passes through the gland, the end being flattened to a spoon-shape; this can be pushed along to the centre of H, or drawn out past the entrance of the side tube of the T. This side tube is closed by a perforated rubber stopper, through which a small glass tube passes bearing a small reflecting prism cemented to the end, which is thus closed up; but in order to allow of the escape of the gases, so that a current may be set up in the apparatus, a hole is blown in the side of this tube near the prism. The outer end of the tube is connected by rubber tubing to another wash-bottle S‴ containing sulphuric acid, and from this again a tube leads to the gas-holder B. Thus the entire apparatus forms a closed circuit and has no inlet or outlet. The gas-holders have each a

Y-tube attached, one branch of the Y leading to the apparatus and the other connecting A with B by means of a rubber tube carrying a clip. The S at the foot of the diagram is a small direct-vision spectroscope, and L is a lens focussing the central parts of the tube H on to the slit of the instrument; both are attached to a strip of hard wood movable horizontally about an axis placed between the lens and the slit. This enables one to instantly push aside the spectroscope into the position shown by dotted lines and observe the glowing tube directly.

To observe the sodium-spectrum, one fills the gas-holder A with some indifferent gas containing no oxygen, or only a trace of that element, such as nitrogen or hydrogen, or ordinary coal-gas. When full it is disconnected with the gas-generator or gas-main, as the case may be, and connexion is made with the apparatus. Next, weights are put on A until sufficient pressure is obtained to drive a current of gas through the wash-bottles, drying-tube, &c. into B. Then the Bunsen is lighted under the porcelain tube, which it presently heats up to a bright incandescence for about two inches of its length. After sufficient dry gas has passed through, and all trace of moisture has gone, the current is stopped by closing the stopcock on A, and a small pellet of sodium is dropped into the steel spoon through the side tube of the glass T, the stopper with the inner tube and prism being removed for this purpose and quickly replaced. The current is then restarted, to drive away any oxygen that may have diffused in by the operation, and at the same time the tube P is gently heated by a spirit-lamp flame until a small faintly luminous flame is seen, indicating combination of the last traces of oxygen with the phosphorus. After this has gone on a sufficient length of time, and the apparatus may be considered to be free from oxygen, water, and carbonic acid, the stopcock on A is again closed and the steel spoon carrying the sodium is pushed into the hot part of the tube H, turned over, the sodium shaken out, and the spoon again withdrawn past the entrance of the side tube. Now the tube carrying the prism is pushed down into line with the tube H, and the white flame of a paraffin-lamp is placed close alongside the glass T, so that a ray of white light can be made to traverse the glowing vapour in H. One may now observe at will the absorption or emission spectrum of the glowing sodium by the simple operation of turning the lamp-flame up or down.

The experiments actually performed with this apparatus may be thus briefly described:—

I. With the porcelain tube strongly heated, a slow current of coal-gas, not specially freed from oxygen, was allowed to circulate in the apparatus, no sodium being admitted. A distinct and fine sodium line was visible in the spectroscope, which increased in brightness when a little air was mixed with the gas, but which gradually faded to invisibility when the phosphorus tube was heated so as to eliminate oxygen.

The explanation of this result appears to be simple enough. The trace of oxygen remaining in the coal-gas combines with the hydrogen when it reaches the hot part of the tube, and the "flame" so formed (which, however, is not visible as such, except when a large quantity of O is present) becomes tinted by the salts of sodium, which in excessively minute quantity are known to be driven off from the porcelain at a red heat, just in the same way as the Bunsen flame outside is tinted. This fine double D line, therefore, may not be the result of heat alone, since it is developed as a consequence of chemical reactions.

II. A pellet of clean sodium was placed in the steel spoon; and the gas—coal-gas—allowed to circulate, the phosphorus being heated. The line seen in Experiment I. was watched, and some time after it had quite disappeared the current was stopped and the sodium pushed into the hot part of the tube. Instantly the central bore of the porcelain was filled with light, which in the spectroscope was found to be perfectly continuous, but crossed by a very wide black line at D. Gradually the continuous spectrum faded, and as it became fainter the dark D line was seen to be bordered with a fringe of light on each side; and as the vapour became less dense, owing to the distillation of the sodium into cooler parts of the tube, the D line went through the changes represented in fig. 3, in the order *a*, *b*, *c*, *d*, finally persisting as a rather wide bright line in which a very fine dark line could usually be made out *. But at any stage of the experiment, the dark central line could easily be extinguished by allowing a gentle current of gas to push back the cooler absorbing layer into the hotter regions. Now the question to be decided was whether this broad bright, hazy D line was or was not the result of chemical activity.

III. In this experiment the phosphorus tube and the drying-tube were cut out of the circuit, the gas-holder A being connected directly with the heating-tube. With the current of gas stopped, the D line appeared as in the last experiment, but observations were somewhat impeded by opaque clouds of oxide which hung about the cooler parts of the tube. When, however, a slow current of the undried gas was allowed to impinge on the sodium vapour, by partly opening the stopcock A, the absorption-line vanished and an intensely brilliant but fine line appeared in its place in the centre of the broad but relatively faint emission-line. This sharply-defined narrow line resembled the ordinary D line seen in flames. It was brighter than the continuous spectrum of the glowing sides of the tube, on which it appeared to be superposed.

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* The dispersion of the spectroscope employed in all the sodium experiments being insufficient to separate the two components of the D line, it is evident that when this line appeared widened the two were really fused into one broad band.

IV. Atmospheric nitrogen was substituted for coal-gas in the gas-holders, and was freed from traces of oxygen and dried before entering the heating-tube by passing over heated phosphorus and through a tube of $CaCl_2$. The phenomena observed on volatilizing the sodium in this gas were in every way the same as in coal-gas. It was subsequently found that the same results could be obtained with unpurified nitrogen, or even with common air, the sodium itself effecting the purification almost immediately on vaporizing, producing at the same time a brilliant flash—in the spectroscope a brilliant but sharply-defined and narrow D line—and clouds of oxide; afterwards showing the broad hazy emission-line and the central black absorption-line, when all the oxygen in the tube had been consumed and the oxide had subsided.

These results appear to me to show that impurities in the neutral gases used are not concerned in the production of the broad hazy emission-line, for when traces of these, particularly oxygen and moisture, are known to be present and are allowed to impinge on the sodium vapour, a line is seen which is fine and sharp, showing that the region of chemical action is only a surface-layer of no great density, whilst the fainter but broad and diffuse D line, always seen when the vapour is undisturbed, evidently originates at a great depth where the vapour-density is considerable and in a region *protected* from chemical action by the outer relatively cool layers giving the absorption-line.

While this central region of the vapour may be considered to be well protected by the outer layers from impurities in the neutral gas employed, there still remains the possibility that the porcelain tube itself reacts with the sodium throughout its heated part, thus furnishing a continual supply of chemical energy; and some support is given to this view of the case from the fact that the bright line cannot be maintained as a wide line indefinitely without a continual addition of fresh sodium, also the tube becomes much corroded, black silicon being deposited inside: thus proving a reaction between the silicates of the porcelain and the sodium.

In the experiments which follow, the effect of such reactions between the tube and the sodium is eliminated by the use of iron tubes in place of porcelain. The first trials were made with a short piece of iron tube about 6 cm. long and 8 mm. bore, bevelled at the ends and fitted between two hard glass tubes of the same diameter, the joints being ground to fit. This made good joints when the iron became red-hot and the glass in contact with it was softened and pressed up tight; but although satisfactory results were obtained in two or three experiments, constant trouble was experienced in the cracking of the glass while cooling. Finally the glass was discarded and a long iron tube prepared (a piece of ordinary $\frac{1}{4}$-inch hydraulic tube). In order to diminish as far as possible the loss of heat by conduction, so as to maintain a high temperature for about 8 cm. in the central part, a number of deep necks were cut in the metal, as shown in fig. 2, and around these necks a thick ring of asbestos-packing was wound and a fire-clay arch placed over all. Thus the Bunsen flame could be concentrated entirely on the central piece of the tube and the temperature could be maintained inside the tube above the fusing-point of fluor-spar and aluminium, but not reaching that of silver. The rubber connexions between the ends of the iron tube and the two T-pieces gave trouble at first, but subsequently it was found that when buried in a thick layer of plaster of Paris they were completely protected from destruction by heat, the large surface afforded by the plaster of Paris forming an effectual radiator and preventing the ends from becoming too hot.

Experiment V.—With the iron tube at a bright red heat, the sodium was tipped out from the steel spoon as before, in an atmosphere of carefully dried coal-gas. Now, if in the previous experiments the D radiation was due to chemical action taking place between the sodium and the oxygen compounds of the porcelain, one ought in this experiment to find, if not an entire suppression of the bright line, at least a striking difference in the radiation. No such difference was, however, to be observed, the intensity remaining precisely the same as before and the sequence of phenomena closely resembling that shown in fig. 3. The various phases there shown were, however, prolonged almost indefinitely in time, as the sodium never became used up as before, and the distillation into cooler parts of the tube proceeded so slowly that it was necessary to allow a gentle current of gas to drive away the denser vapour giving a continuous spectrum before the D line itself could be studied. Also throughout the experiment the dark absorption-line was more intense than in porcelain, and it could easily be observed after six hours of continuous heating, when even the emission-line had become relatively narrow. This naturally follows from the consideration that in the iron the temperature-gradient on each side of the central red-hot part of the tube is much less steep than is the case when porcelain or glass is used, and consequently there is a much greater thickness of relatively cool vapour through which the emission-line is seen.

Under the conditions of these experiments, therefore, the bright D line appears to be quite uninfluenced either by the nature of the neutral gases used and the impurities they may contain, or by the material of which the heating-tube is composed: iron giving exactly the same results as porcelain. It would hardly be safe, however, at this stage of the inquiry to infer that chemical reactions are not concerned in the production of the light; for it would be argued that, as iron becomes slightly porous at a red heat, oxygen, or at any rate some of the gaseous constituents of the Bunsen flame, might find their way into the tube by diffusion from outside, and in this way maintain a continual reaction with the sodium vapour.

In order to diminish the possibility of this diffusion inwards affecting the results, a constant pressure of a few millimetres above atmospheric pressure is maintained within the tube, and if gases diffuse in at all it must be in opposition to the outward diffusing hydrogen. It has been pointed out to me, however, by Prof. Smithells that in dealing with the D line we are dealing with a reaction that is sensitive to $\frac{1}{180,000,000}$ of a grain of sodium. It is only necessary to suppose, therefore, an equivalent amount of oxygen or other reacting body to be continually present in the tube to determine the D radiation.

While I am not prepared to deny the possibility of such minute traces of oxygen or other bodies constantly finding their way into the middle of the sodium vapour, I consider that any reactions so caused could under no circumstances produce the broad ill-defined line actually observed. At the most a fine double D line would be seen similar to that of a flame tinted with a salt of sodium, where the density of the reacting molecules is not great. Moreover, if reacting bodies were diffusing in from outside the tube—the absorbing layer of the sodium vapour itself forming an effectual barrier in other directions—the action would be greatest in an annular region in contact with the sides of the tube where the incoming molecules first encountered the sodium. This should cause a brightening or widening of the D line at each end *. But there is no such inequality seen: the line is quite uniform in width and brightness throughout its length; showing that if chemical reactions are producing the light, the reacting

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* The D line with the optical arrangement employed represents a section of the space inside the hot part of the tube.

molecules must be uniformly distributed throughout the mass of vapour.

The most telling argument, however, and one which, taken alone, appears to me to prove beyond a doubt that the D radiation under these conditions is the direct result of the heating, is that derived from a comparison between the emission and absorption spectra.

To effect this comparison, the lamp and reflecting prism previously described are brought into operation, and a beam of white light is made to traverse one side of the heated tube, so that one portion of the slit of the spectroscope is illuminated by transmitted white light, whilst another contiguous portion is illuminated by the D radiation alone. Under these circumstances the absorption and emission spectra appear side by side in the field of view, and may be readily compared.

Figs. 3 and 4 show the corresponding phases of these spectra (denoted by letters of the alphabet). It will be noticed that the emission-line or band in *c*, *d*, and *e* is represented as of the same width as the absorption-band. Careful observation under various conditions as to density shows that, excepting for the dark line in the centre, the bright D line is in every respect the exact counterpart of the absorption-line, whether the broad hazy band of the dense vapour is studied, or the relatively narrow line seen with more attenuated vapour.

Assuming, then, that the width of both absorption and emission lines is determined by the molecular density of the absorbing and emitting vapour, it follows that in the densest region every molecule that is concerned in the absorption is also concerned in the radiation. In other words, practically every molecule in the hot part of the tube contributes its share to the radiation. But it is surely impossible to suppose that every molecule, or even a large proportion of the molecules, is continually undergoing chemical change. The supply of oxygen or other reacting bodies—supposing they do gain access to the sodium—will never be equal to even a small fraction of the demand; also, if oxidation is proceeding, one would expect to find traces of oxide forming after several hours. But the heating may be continued for six hours at the least without touching the apparatus, and at the end of this time the D line, with its central absorption-line, is seen as clearly as at the beginning, there being no trace of any opaque clouds of oxide such as are always seen when traces of oxygen are known to be present in the tube.

There seems no possible alternative, therefore, to the obvious and simple explanation which ascribes the radiation to heat alone. If it were assumed that there exists diffused throughout the sodium vapour some substance capable of setting up chemical reactions, it might indeed be imagined that a kind of cyclical process of alternate combination and dissociation takes place, the energy supplying the radiation being derived indirectly from the heated walls of the tube: these alternate changes being determined by differences of temperature in the reacting molecules, the cooler combining and the hotter dissociating, or *vice versâ.* But it is practically certain that under the conditions of these experiments there must always be a large excess of sodium molecules over any others likely to produce such reactions, unless, indeed, hydrogen or nitrogen were to behave in this way towards sodium, and the spectroscopic evidence, as just explained, implies that *all* the free sodium molecules are concerned in the radiation.

Or perhaps it may be further argued in support of the "chemical" origin of the radiation, that the sodium molecule is itself undergoing alternate dissociation and recombination. The reasons already given against this view in the case of iodine apply even more forcibly in this instance. Thus, if the radiation were due to such action, the intensity should follow the curve representing the change of relative vapour-density with temperature, rising to a maximum at the turning-point in this curve—indicating the greatest interaction between the atoms and the molecules—but falling away to zero when the point of complete dissociation is reached. Now the most reliable recent determinations of the vapour-density of sodium indicate that at about the temperature of melting cast-iron the vapour is entirely monatomic *: therefore, if we assume that at the lowest temperature of my experiments the atoms are more or less aggregated, the relative intensity of the D line, compared with the continuous spectrum of the glowing sides of the tube, should change as the temperature is increased,—it should get brighter or fainter according as the actual temperature of dissociation is above or below the initial temperature of my experiments; and it should cease altogether if the temperature be raised to the point where the vapour becomes entirely monatomic.

But as a matter of fact there is no such change of relative intensity. As the temperature is increased from the point where the radiation begins to be seen, the D line follows strictly the continuous spectrum of the glowing tube: from the lowest to the highest temperature (a range of some 300 C. degrees), the gaseous radiation increases in intensity exactly in correspondence with the radiation from the solid, always keeping the *same* intensity (so far as the eye can judge) as the spectrum of the glowing tube.

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* A. Scott, Proc. Roy. Soc. Edinb. xiv. p. 410.

Origin of the Continuous Spectrum.

There remains to be considered the continuous light seen when the sodium is first volatilized, and before the broad D emission-line appears (fig. 3, *a*). After a number of experiments, made under various conditions as to the purity of the coal-gas or nitrogen employed and density of the sodium vapour, I conclude that this radiation is really due to free sodium, and that it always appears when the vapour is above a certain density. It is well known that dense sodium vapour gives a remarkable banded absorption-spectrum *. In the experiment alluded to, I have studied the continuous emission-spectrum in relation to this banded absorption, and find that they are intimately connected: thus, when the sodium is first volatilized and a bright glow fills the tube, the vapour appears a splendid violet colour by transmitted light; it is in fact opaque to all rays except the violet; gradually, however, green rays begin to be transmitted (fig. 4, *a*), then red (fig. 4, *b*); the dark space between the green and the violet is now seen to be made up of a large number of black lines (close together with the low dispersion employed), these rapidly decrease in intensity as the vapour diffuses along the tube and becomes less dense, while the black band blotting out the yellow assumes the usual appearance of the wide D absorption-band †. The continuous *emission* glow persists through these progressive changes in the absorption, but becomes gradually fainter, and as the last traces of the absorption-lines in the blue disappear it fades away almost entirely, leaving behind, so to speak, the broad bright emission-band at D, the exact reverse of the absorption-band, except for the black line filling up the centre, due to relatively cool vapour in the nearer part of the tube.

It seems, therefore, that dense sodium vapour, like iodine and other *coloured* vapours giving banded absorption-spectra, emits when in this state light of all wave-lengths, and that the change to discontinuous emission is determined by a reduction of density. There are indications, however, that at higher temperatures the continuous light would give place to bands corresponding with the absorption-bands, just as iodine is said to give a banded emission spectrum when heated externally to a high temperature (Salèt, *Traité sur Spectroscopie*, p. 174) *. For if the continuous light is watched at the highest temperature attainable with this apparatus, it is seen not to fade equally in all parts of the spectrum,—a stage is reached (see fig. 3, *b*) when, in addition to the D emission-line, a green line appears in the place of a conspicuous absorption-line, and a faint glow remains in the blue corresponding to the absorption-bands in that region (figs. 3–4, *b*).

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* *Vide* Roscoe & Schuster, Proc. Roy. Soc. xxii. p. 362.

† A curious phenomenon may be seen when a current or gust of gas is allowed to drive the dense vapour along the tube. The colour of the vapour seen by transmitted light suddenly changes from green to a splendid ruby-red. This is not due to a change in the character of the absorption-spectrum, but may be explained as an effect of refraction: the sodium vapour, being blown out more in the centre than along the sides of the tube, acts like a prism, refracting the blue and green rays radially from the centre, the red alone—being least deviated—passing out at the end of the tube. This effect is more obvious with hydrogen than with nitrogen.

XLVII. *Intelligence and Miscellaneous Articles.*

ON THE ROTATIONAL COEFFICIENTS OF THERMAL CONDUCTIVITY IN CRYSTALS. BY M. CHARLES SORET.

The method used has been pointed out in a previous note (*Archives de Genève*, 1893, xxix. p. 355).

Heating by the method of Jannettaz a point on a face not perpendicular to the axis of rotation in a crystal in which the coefficients in question are not zero, isotherms should be obtained which are not symmetrical in reference to that diameter which coincides with the projection of the axis of rotation.

The crystals were mounted and centred at the end of a vertical axis provided with screw motions for setting the face horizontal. A small platinum sphere heated by an electrical current is applied against this face at a point A on the prolongation of the vertical axis.

Isotherms were obtained in the usual way, taking care to turn the crystal steadily and regularly during the heating so that this was symmetrical about the point A. This point, the intersection of the face investigated and the axis of rotation, was thus without any possible error in the centre of heating.

After obtaining the isotherm it was examined, without touching the adjustment, by means of an eyepiece with a micrometric scale. The crystal being first placed with its rotational axis in the plane of incidence, a rotation of 180° about A should modify the points of intersection of the micrometer and the isotherm, if this was symmetrical as regards the centre of heating.

Now no appreciable disymmetry could be observed any more than by the other methods previously employed. Small variations, evidently accidental, alter the direction from one observation to another on the same crystal, amounting to $\frac{1}{30}$ to $\frac{1}{50}$ of the diameter of the curves. Irregularities of the same order were observed on isotropic plates and on faces of crystals, in which no constant deformation of the isotherms could be foreseen.

The researches were made on crystals of dolomite of Binn (face of the prism), and of Traverselle (face of the rhombohedron): on crystals of erythrite and on apatite of the Pfitschthal (face of the prism). The existence of coefficients of rotation in the crystals appears therefore more and more improbable.—*From the Archives de Genève,* communicated by the Author.

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* If iodine is heated in a hard glass tube in a furnace until the glass begins to fuse, the colour of the glowing vapour changes from yellow to pale greenish white. This probably indicates the change to a discontinuous emission.

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XLVIII. *On the Scale-Value of the late* Dr. Joule's *Thermometers.* *By* Arthur Schuster, *F.R.S.*[*]

[Plates V. & VI.]

IN order to bring the results of Joule's researches on the mechanical equivalent of heat into relation with more modern experiments on the same subject, it is necessary to determine the scale-value of Joule's thermometers in terms of some easily reproducible standard.

We possess already a comparison by Joule himself of his thermometer with one used by Rowland, who has corrected Joule's result to the scale of his own air-thermometer.

Some doubt may still exist, however, as to the true scale-value of these instruments, partly owing to the fact that we have no information how the comparison between Joule's and Rowland's thermometers was conducted, and partly because we do not know to what degree of accuracy Rowland's air-thermometer would agree with that of the Bureau International des Poids et Mesures, which for the present must be considered as the standard.

The historical importance of the instruments used by Joule seemed to make it desirable therefore to subject them to a more extended investigation. The request which I made to Mr. B. A. Joule to allow me the use for a short time of his late father's thermometers was met by a most ready compliance, and I beg to offer him my best thanks for the opportunity which he has given me of examining these interesting relics.

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[*] Communicated by the Author.

The two thermometers which I had at my disposal were those called A and D in Joule's published papers; they were made and calibrated by Dancer in 1844. The thermometer D includes both the freezing- and boiling-point, while A only reaches to a little above 30° C.

In order to show to what extent Joule trusted these instruments, I quote the passages in his papers in which he refers to them:—

"My thermometers were constructed by a method very similar to that employed by Regnault and Pierre. The calibre of the tube was first measured in every part by passing a short column of mercury along it. The surface of the glass having then been covered with a thin film of beeswax, the portions of tube previously measured were each divided into the same number of parts by a machine constructed for the purpose. The divisions were then etched by means of the vapour of fluoric acid. Two thermometers were employed in the present research, in one of which the value of each space was $\frac{1}{18\cdot14}$, in the other $\frac{1}{23\cdot38}$ of a degree Centigrade. A practised eye can easily estimate the tenth part of each of these spaces; consequently I could by these thermometers observe a difference of temperature not greater than 0°005." (Phil. Mag. [4] vol. iii. p. 481; Collected Works, vol. i. p. 214.)

"The thermometers employed had their tubes calibrated and graduated according to the method first indicated by Regnault. Two of them, which I shall designate by A and B, were constructed by Mr. Dancer of Manchester; the third, designated by C, was made by M. Fastré of Paris. The graduation of these instruments was so correct, that when compared together their indications coincided to about $\frac{1}{100}$ of a degree Fahr. I also possessed another exact instrument made by Mr. Dancer, the scale of which embraced both the freezing- and boiling-points. The latter point in this standard thermometer was obtained, in the usual manner, by immersing the bulb and stem in the steam arising from a considerable quantity of pure water in rapid ebullition. During the trial the barometer stood at 29·94 inches, and the temperature of the air was 50°, so that the observed point required very little correction to reduce it to 0·760 metre and 0° C., the pressure used in France, and I believe the Continent generally, for determining the boiling-point, and which has been employed by me on account of the number of accurate thermometrical researches which have been constructed on that basis. The values of the scales of the thermometers A and B were ascertained by plunging them along with the standard in large volumes of water kept constantly at various temperatures. The value of the scales of thermometer C was determined by comparison with A. It was thus found that the number of divisions corresponding to 1° Fahr. in the thermometers A, B, and C were 12·951, 9·829, and 11·647 respectively. And since constant practice had enabled me to read off with the naked eye to $\frac{1}{20}$ of a division, it followed that $\frac{1}{200}$ of a degree Fahr. was an appreciable temperature." (Phil. Trans. 1850, pt. i.; Collected Works, vol. i. p. 302.)

On the Centigrade scale the figures given in the last quotation would be 23·312, 17·692, 20·965. This allows us to identify the second thermometer of the first quotation with the one called A in all subsequent papers.

"The thermometer used to indicate the temperature of the calorimeter was the same which I employed in my former experiments. Those designated A and D were calibrated with great care. I have recently compared them together at 50 different temperatures between 32° and 80° Fahr., the result being that, if the less sensitive was assumed to be correct, the other, or A, nowhere appeared more than 0°·023 in error; but taking averages for each consecutive 10°, this error amounted to no more than 0°·008." (Phil. Trans. 1878, part ii.; Collected Works, vol. i. p. 636.)

Description of the Thermometers.

The two thermometers which I had at my disposal were those called A and D. The form and size of their bulb and the width of the stem are shown in figs. 1 and 2, the former representing in natural size the bulb and beginning of the stem of the thermometer A, and the latter that of D. The diameters of the two stems are 0·7 centim. (A) and 0·75 centim. (D). The length of the stems 87 centim. (A) and 86 centim. (D). The volumes of the bulbs may be calculated approximately from their shape, and are found to be 4·9 cub. centim. and 3·8 cub. centim. respectively.

As the thermometer A was the one always employed in calorimetric measurements, it is this instrument which is of chief interest to us now. From the pressure coefficients of the thermometer, we may approximately calculate the thickness of the glass walls of the bulb, in the manner indicated by Guillaume. The calculation can be carried out if the bulb is cylindrical or spherical, and cannot strictly be applied to such a shape as that shown in fig. 1. But I find that, assuming the bulb to be cylindrical, the pressure-coefficient gives a thickness of 0·09*, while on the assumption that it is spherical the calculated thickness of glass is 0·076, so that the result is almost the same, and we are not probably far wrong in taking ·08 as the approximate thickness. Taking account of this value and the external volume, I find the volume of mercury to be about 4 cub. centim., and from the length of one degree of the stem obtain the radius of the bore approximately as ·009. These numbers do not lay claim to any accuracy, but they are sufficient to give us an idea of the principal quantities involved in the construction of this thermometer.

Fig. 1.

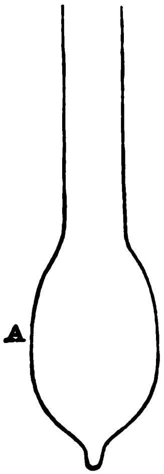
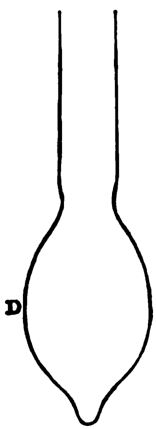


Fig. 2.



As the thermometer was calibrated before graduation, the distance between the divisions will give us some idea as to the regularity of the bore. In Table I. the first column gives the division of the thermometer, and the second, in millimetres, the corresponding distance from the centre of the reservoir, the third column gives the differences between the numbers of the second, and the numbers of this column are therefore inversely proportional to the mean area of the bore at different points of the thermometer.

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* All results, unless otherwise stated, are given in centims.

TABLE I.

Division.	Distance from centre of bulb.	Distance between successive intervals of 50 divisions.	Pressure correction in degrees.
0	9·2	......	0°·0234
23·3 (zero)	11·1	......	·0284
50	13·4	4·2	·0343
100	17·7	4·3	·0453
150	22·2	4·5	·0567
200	26·7	4·5	·0683
250	31·4	4·7	·0802
300	36·1	4·7	·0922
350	40·8	4·7	·1042
400	45·6	4·8	·1165
450	50·6	5·0	·1292
500	55·7	5·1	·1423
550	60·9	5·2	·1556
600	66·0	5·1	·1686
650	71·2	5·2	·1819
700	76·5	5·3	·1955
750	81·8	5·3	·2089

To calculate the pressure correction we require the distances from the centre of the bulb, but there must of course be some uncertainty as to the point which is chosen as centre. The figures in the third column were obtained by direct measurement and are not affected by the same uncertainty. It will be seen that the bore is conical, gradually diminishing in diameter. The mean cross-sections near the two ends of the tube differ by about 20 per cent.

In addition to the differences in the length of division intended to correct for the changes in the bore, there are also not inconsiderable inequalities which are evidently due to faults of graduation. These irregularities are quite visible with the naked eye, two successive intervals differing occasionally by as much as the tenth part of their own length. Owing to this fact the error of a single reading of this thermometer A may amount to 0°·004 C. quite independently of the general errors of calibration. It must be remembered of course that at the time the thermometers were made such a quantity was not considered to be of any importance, so that the divisions were sufficiently accurate for the purposes for which they were originally intended.

The Fundamental Points.

As regards the thermometer D, Joule has supplied us with the following information :—

"The freezing-point of the standard D had risen from 13·3 divisions of its scale in 1844 to 15·14 in 1877. I think it probable that the boiling-point of this thermometer, if kept constantly at this temperature, would in the course of time fall as much. The five careful determinations of this boiling-point referred to 30 bar. and 60° are respectively 706, 706·4, 706, 705·9, and 706·15—mean 706·09. Subtracting 1·84, 704·25 will be the probable ultimate reading, from which if we take 15·14 we shall have 689·11 as the range between the fixed points cleared from the effects of imperfect elasticity of the glass. Mr. E. Hodgkinson has pointed out (Brit. Assoc. Report, 1843, p. 23) that the 'set' of imperfectly elastic bodies is proportional to the square of the force applied, therefore the effect of imperfect elasticity in the glass of the thermometers will be insensible for the small ranges used in the experiments, and the factor 3·3822 for reducing the indications of D to those of A may be confidently relied on.

"We have therefore

$$\frac{180}{689{\cdot}11 \times 3{\cdot}3822} = 0^{\circ}{\cdot}07723$$

as the most probable value of one division of A. In my former papers the number was taken as 0°·077214, which is so near that I shall continue to use it, trusting by long-continued observations of the fixed points to give it ultimately greater accuracy, and also, by experiments above indicated, to state it in terms of the absolute interval between these points." (Phil. Trans. 1878, part ii.; Collected Works, vol. i. p. 636.)

It will be noticed that the actually *observed* difference between the freezing- and boiling-point is 690·95 divisions, but that Joule somewhat arbitrarily reduced this by 1·84 divisions, thus altering the fundamental interval by over a quarter per cent. It seems curious that no one should have directed his attention to this point, which to all appearance causes an error in the scale-value of his thermometer, and would make his equivalent come out too low by ·0027 of its own value.

If we collect together the scale-values of the thermometer A, given by Joule in different places, we find :—

In the paper communicated to the French Academy in 1846	one division = ·042772
In the paper read before the Royal Society in June 1849	„ ·042897
In the paper read before the Royal Society in Jan. 1878	„ ·042902
In the last mentioned paper, calculated from the actually observed boiling-point	„ ·042791

It will be seen that the last value nearly agrees with the first; the point to be explained therefore is the high value of the second number. It is possible that a correction similar to that of the last paper was already then applied, and as we have reason to believe that a great part of the change of zero took place in the first four years, we may account for certainly half the difference in this way. The point is not now of great importance, because the scale-value of A must be obtained quite independently of Joule's assumed interval for his standard. Joule's own value depended not only on that interval but also on the correct calibration of his standard. From the method of calibration employed, an error quite as large as that caused by the wrong value of the boiling-point might easily be introduced. Nevertheless a re-determination of the distance between boiling- and freezing-points seemed to me to be of interest, especially as the depression of the zero might give some indication as to the nature of the glass of which the thermometer is made.

When the thermometer came into my possession there was a large bubble of air in the bulb, and the mercury in the stem broke into pieces when attempts were made to drive the bubble into the upper reservoir. I finally succeeded, however, in removing it, but the experiments on the boiling-point were always a little difficult as the mercury when placed in steam had a great tendency to distil into the upper parts of the stem. In order to see that the thread was continuous the thermometer had to be inverted occasionally, the mercury running into the reservoir, and small pellets sometimes remained there on re-inverting, so that no value is to be attached to the actual position of the zero points observed; though the quantity of mercury separated was always so small that the distance between the freezing- and boiling-points could not be affected. Table II. gives the observations made:—

TABLE II.

Date.	Height of Barometer.	Freezing-point before experiment.	Freezing-point after experiment.	Interval.		Depression of zero.
				a.	*b.*	
April 7, 1892.	759·1	15·04	14·35	690·79	691·48	·69
May 11, „	769·1	16·58	16·04	689·63	690·17	·54
May 30, „	759·7	4·97	4·46	690·97	691·48	·51
June 22, 1894.	766·0	9·88	9·08	690·69	691·49	·80
					Mean………	·64

The agreement between the experiments, excepting the second, is better than could have been expected, and accident must have played some part in giving these practically identical numbers. The first and third determinations were made by myself, the fourth by Mr. J. R. Ashworth, the second by another observer, and there must be some error in it which could not afterwards be traced. The intervals are given in 2 columns—(*a*) is the interval calculated on the old method of taking the freezing-point first, while (*b*) is that now generally employed, the reading at the boiling-point being compared with the reading at the freezing-point taken immediately afterwards. The difference between the number so obtained and Joule's interval (690·95) gives the depression of zero as ·53, agreeing fairly well with that found directly by the above experiments. The interval (*a*) is also seen to agree with Joule's value. The time the thermometer was kept exposed to the temperature of boiling water varied from a quarter of an hour to several hours. In the first three experiments the depression seemed to increase with the time of exposure, but in the last experiment that time was only about fifteen minutes, *i.e.* shorter than in the other cases; the large depression may be due to a diminution of the column by distillation.

It appears, therefore, that the depression of the zero is less than 0^{c}·1. It approaches that observed in Jena or French hard-glass thermometers, and is considerably smaller than that found with modern English glass.

The Thermometer A.—This thermometer does not include the boiling-point, but its freezing-point is of interest, as it is probably unique in having been watched for a period of over 50 years. Joule furnishes us with data showing the gradual rise of the zero from April 1844 to March 4, 1873 (Collected Works, vol. i. p. 558). In the communication he presented to the Manchester Literary and Philosophical Society, he refers the rise to the first observed zero without giving the actual readings, so that this short paper does not allow us to judge how far the present zero is above that of 1873. Fortunately, we can indirectly supply the deficiency. For in his comparison with Rowland's thermometer (Proc. Amer. Acad. vol. xvi. p. 38) the reading of the zero is stated to be 22·62. Rowland's thermometer was sent to Joule in the summer of 1879, and the results were communicated to the American Academy in March 1880. The comparison must have been made at an intermediate date, and can therefore be identified, for in the above-mentioned communication only one comparison is mentioned between January 1877 and December 1882, and that one in November 1879, when the zero stood 12·92 divisions above that of the first observation. Taking the original zero to be 9·7, the complete series now is as follows :—

TABLE III.

Date.	Zero.	Date.	Zero.
April 1844	9·7	February 1873...	22·2
February 1846...	15·2	January 1877 ...	22·41
January 1848 ...	16·3	November 1879...	22·62
April 1848	16·6	December 1882...	22·96
February 1853...	18·5		
April 1856	19·2	April 1892.........	23·36 (17°)
December 1860...	20·8	April 1893.........	23·31 (17°·6)
March 1867	21·5	June 1894	23·35 (17°)
February 1870...	21·8		

I have taken a considerable number of readings of the zero-point since the beginning of the year 1892. They vary of course with the temperature to which the thermometer was exposed. The determinations were made in an apparatus similar to that described by Guillaume, the thermometer being immersed in a mixture of scraped ice and distilled water. Great care must be exercised in the readings, for, owing to the large size of the bulb and the long time taken by the thermometer to reach a steady state, the results are easily vitiated by an accumulation of water. No correction was made for the pressure due to the surrounding mixture, as probably Joule took no account of that pressure, nor would the correction be significant for our purpose. The readings are arranged in groups according to the temperature at which the thermometer had been kept, and I have divided them into three periods.

First Period.

March 30 to April 7, 1892.

Average temperature to which the thermometer had been exposed.	Number of Observations.	Mean zero.
° 8·6	2	23·47
12·9	4	23·41
17·1	2	23·36
30·9	1	23·05

Second Period.

March to June 1893.

° 13·7	1	23·19
17·6	3	23·31
23·3	3	23·32

Third Period.

June 22, 1894.

° 17	1	23·35

The first observation of the second series does not fit in very well with the others, but if it is remembered that a tenth part of a division means only 0°·004, the general agreement must be considered satisfactory, and the first series, which is perhaps the one in which the greatest care was exercised, shows the gradual lowering of the freezing-point very decidedly. The numbers show that the changes of zero are no longer appreciable. I have added to Table III. those of my observations which were taken after the thermometer had been exposed to about 17°.

The Pressure Correction.

As the chief object of this investigation was to find the scale-value of the thermometer A under the conditions holding in Joule's experiment, the most natural manner of proceeding would have been to compare it in the vertical position with some standard instrument. Owing to the great length of the thermometer it was not found possible, however, without much inconvenience to construct a vessel into which it could entirely be plunged vertically, and if only partially immersed the uncertain stem corrections would take away considerably from the accuracy of the comparison. After a few trials which gave no satisfactory results, it was resolved to carry out the comparisons in a horizontal position and to determine independently the correction which has to be applied in order to reduce the readings to the vertical. This correction owes its origin to the expansion of the thermometer-bulb through the internal pressure of the mercury column. It is determined by measuring the effect of *external* pressure. If the addition of an external pressure p produces a rise of the column of mercury equal to $p\beta_e$ degrees, and an equal internal pressure produces a fall $p\beta_i$, then two equal pressures p applied from both sides would produce a rise equal to $p(\beta_e-\beta_i)$, but this rise may be calculated in another way. A hydrostatic pressure p will alter the volume of the vessel by $p\kappa_g$, but the apparent contents of the vessel as measured by the mercury thread will only diminish by $p(\kappa_g-\kappa_m)$ where κ_g and κ_m are the coefficients of cubical compression of glass and mercury respectively.

We thus obtain the equation

$$\begin{aligned}\beta_i&=\beta_e+(\kappa_m-\kappa_g)\\&=\beta_e+0{\cdot}000154\,\frac{\text{degrees}}{\text{centim. of mercury}}\text{*}.\end{aligned}$$

This equation is deduced by Guillaume for the case of thermometers with cylindrical bulbs, but, as is shown by the preceding deduction, it holds quite generally.

The apparatus used for the determination of the pressure corrections is shown in Pl. V. fig. 3, and, as will be seen, is almost identical with that described in Guillaume's book. The thermometer is suspended in a long glass tube T, into which sufficient mercury is introduced to cover the bulb; the rest of the tube is filled with glycerine in order to reduce the air-space as much as possible. Side tubes, with stop-cocks A and B, are led into the upper end of T—one communicates with the outer air, the other with a pressure-gauge, a Winchester quart vessel K, and a water-pump. If the cocks A and B are closed and the pump set to work, it will gradually exhaust the vessel K, and when the pressure is sufficiently reduced B is suddenly opened. Owing to the large volume of K, compared to the air-space in T, the pressure-gauge remains sensibly unaltered, and the reduction of pressure can at once be observed on the thermometer, which is read off by a kathetometer telescope. The pressure can be restored to the atmospheric pressure by closing B and opening A.

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* Guillaume, *Thermomètrie*, p. 103.

I have found it convenient to proceed in the observations rather differently from the manner indicated by Guillaume. The tube T is placed in a calorimeter containing about a litre and a half of water, and that again is surrounded in an outer jacket. The latter is filled with water about 2° above that in the calorimeter, so that the thermometer is kept slowly rising. The air-space in T being exhausted, a few observations are taken at measured intervals of time, air is suddenly admitted, and a further series of readings are taken, as in the following example:—

Observation.	Time.	Reading.	Reading Pressure Gauge.
	h m		
1.	2 15·5	158·85	72·6
2.	16	158·85	
3.	16·5	159·05	
4.	17	159·17	
5.	17·5	159·30	
6.	18	159·35	
7.	18·5	159·40	
8.	19	163·60	0
9.	19·5	163·70	
10.	20	163·75	
11.	20·5	163·85	
12.	21	163·95	
13.	21·5	164·05	
14.	22	164·20	

Taking the arithmetical mean between the first seven observations, it is found that the average temperature corresponding to the time 17^m was 159·139, and by combining the observations in pairs in the usual fashion we deduce the average rate of rise per interval as ·108. Hence

$$159{\cdot}139+4\times 10{\cdot}8=159{\cdot}571$$

gives the calculated reading at 2^h 19^m, but after the seventh reading the air was admitted, so that the last seven observations were taken at full atmospheric pressure. The reduction being made in exactly the same fashion, another reading is deduced for the time 2^h 19^m, viz., 163·583. The difference betwen the two gave 4·012 divisions of the thermometer as the effect of a change of pressure of 72·6 centim. A number of observations of a similar character were taken and are collected in Table IV. They were always so combined that the observation at atmospheric pressure *followed* that at reduced pressure. Otherwise a fall of the thermometer would have taken place, and owing to the sticking of the thread the first few observations would have been uncertain.

Table IV.

Date.	Fall in divisions per cm. of mercury pressure.
April 28, 1892	·0564
" "	·0567
Feb. 22, 1894	·0563
	·0559
	·0548
Mean	·0560
Mean excluding last number	·0563

The observation which is quoted in full above is the one which shows greater irregularities in the rise than the others, and it gave the result (·0548) which differs most from the mean. Part of the discrepancies between the different observations is no doubt due to the irregularities in the graduation of this thermometer, but the result is sufficiently accurate for the purpose for which it is intended.

Reduced to degrees, the final results are as follows :—

	In degrees per cm. of mercury.
Coefficient of external pressure	0·002400
" internal "	0·002554

Knowing the distance of any scale-division from the centre of the reservoir, we may calculate the corresponding pressure correction. A table was calculated once for all, giving in this way the differences between the readings of the thermometer in the horizontal and vertical positions for every 50 divisions. The numbers are given in the last column of Table I. It will be noticed that an error of 1 per cent. in the pressure correction would cause a difference of less than 0°·002 on a range of over 30°, which difference of course would be quite inappreciable.

Some experiments were made to find how much the thermometer A lagged behind when placed in water the temperature of which was uniformly rising. They were carried out according to the manner described by Thiesen*, and gave sufficiently consistent results showing the time constant to be 12ˢ.

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* Guillaume, *Thermométrie*, p. 187.

The Apparatus used in the Comparison of Thermometers.

The comparison of the thermometers was carried out in a bath made of sheet-iron having a length of 114 centim. and width and depth of 20 centim. This bath was placed for protection inside a wooden box, on the bottom of which it rested upon two ribs covered with guttapercha, so that the inner vessel was practically insulated thermally. The wooden box K is shown in Pl. VI. fig. 4, placed on two stools and in front of a table T. A frame FF fitted into the bottom of the bath and carried 38 turns of No. 21 nickel wire, the ends of the wire being brought to binding-screws placed at two of the corners of the outer box. With a suitable electric current passing through the wire, the temperature of the water in the bath could either be kept constant or increasing at a desired rate within a range from 1° to 15° above the temperature of the room. The whole of the interior of the bath, also the frame, and wire were coated with white paint. A tank of water of this kind containing over 40 litres cannot with any reasonable amount of stirring be kept at a sufficiently uniform temperature. The bulbs of the thermometers were therefore placed into a small copper box B, within which the stirring was much more efficient. The box was 15 centim. in breadth and 10 centim. deep, and was rigidly suspended from a wooden cross-bar resting on the side of the case. Vertically down the centre of the box passed a spindle carrying a double 3-bladed screw-paddle; one of these paddles was fixed just below the bottom of the box, and the other just inside the box, as shown in the figure. There was a further paddle at the other end of the bath, the power being supplied by two Cuttriss motors. The stirring was sufficient to secure a very approximately uniform temperature all over the bath. The box B sheltered the thermometers from outside radiation, and protected them against jets of hot water coming from the heated water, the paddle below the box being specially intended to prevent irregular heating of the box. The water inside B was thoroughly stirred, a mere rotation of the water being prevented by oblique diaphragms fixed to the sides. One further precaution was found advisable. Owing to evaporation and radiation the water lost heat at its upper surface, and the thermometers had to be protected against an inflow of cold water through the opening through which the spindle passed. This was done by a horizontal disk H fixed to the spindle, and by covering the whole box as far as possible with asbestos. The thermometer bulbs passed through a window W 3·3 centim. wide, cut into one side of B, and a sliding shutter of thin brass served to close the window partially so that there was only very little, if any, circulation of water between the inside and the outside of the box.

The thermometers were read by a small microscope M which could be moved parallel to itself along the upper edges of the outer vessel. The microscope was mounted so that it also had a free motion at right angles to the length of the box. This double motion allowed it to be moved quickly above the ends of the threads of any two thermometers to be compared. Latterly two microscopes were used, one for each of the thermometers. The water was covered by a sheet of glass, which kept the surface calm in spite of the disturbance set up by the stirring. The thermometers were supported in triangular grooves cut into two adjustable brass uprights P, P. Care was always taken to set them horizontally by first placing a straight edge across the uprights and levelling. This horizontal position is not necessary when the thermometers are transparent, so that their divisions can be read either from the front or from the back, as errors of parallax are thus eliminated. But when this cannot be done the reading microscope must be placed at right angles to the thermometer, and then it is most convenient to have one vertical and the other horizontal. The optic axis of M was put into the vertical position by keeping at a proper distance in the bath a horizontal glass-scale silvered at the back. When the adjustment is correct the two images of the division which is in the centre of the field of view should cover each other, otherwise there is parallax. As the object of the adjustment is to avoid parallax in the reading of the thermometers, this method answers very well if the glass-scale is about 2 millim thick. It is instructive to notice how great the danger of error due to parallax is when sufficient care is not taken to read only in the centre of the field of view.

The Method of Comparison and Reduction.

Two observers were found necessary to carry out a satisfactory comparison, one calling out the time at regular intervals and taking the notes, the other reading the thermometer. An example will show the method adopted.

On June 20, 1893, a comparison was made between Joule A and a Tonnelot Standard No. 4929. Both thermometers were kept in the bath at a temperature of 18° for several hours, then their freezing-point was determined and found as follows :—

Tonnelot, No. 4929 :	0·0082	(mean of 4 observations).
Joule A :	28·23	(„ 6 „).

The air of the room was above that of the bath, the temperature of which was slowly rising without the use of an electric current. The thermometers being replaced in the bath, readings were taken alternately every quarter minute, first with the divisions in front of the thread, and finally with the divisions behind. The numbers obtained were as follows:—

Tonnelot.

(Divisions in front.)

h	m	s	
4	9	15......	18·509
		45......	11
	10	15......	14
		45......	16
	11	15......	21
		Mean......	18·5142

Joule.

(Divisions in front.)

h	m	s	
4	9	30......	458·61
	10	0......	·63
	10	30......	·66
	11	0......	·69
		Mean	458·648

Tonnelot.

(Divisions behind.)

h	m	s	
4	12	45......	18·551
	13	15......	53
		45......	61
	14	15......	72
		45......	74
		Mean	18·5622
		General Mean	18·5382

Joule.

(Divisions behind.)

h	m	s	
4	13	0......	459·06
	13	30......	·16
	14	0......	·39
	14	30......	·48
		Mean	459·273
		General Mean	458·961

The zeros were now again determined and found :—

Tonnelot 0·0075 (mean of 4 observations).
Joule A 23·192 („ 6 „).

A small correction is applied to the Joule thermometer for the lagging behind, and we thus got for corresponding temperatures :—

Tonnelot	18·538	Joule	458·99
Zero . .	·008		23·21

In the first series of comparisons the Joule A was compared in this way with the Tonnelot thermometer. The latter had been calibrated and investigated at the Bureau International des Poids et Mesures, so that its indications could at once be reduced to the normal scale. The results of the comparison are given in Table V. The first column gives

TABLE V.

I. T_T.	II. Joule A.	III. Joule A, −23·33.	IV. Joule A, ×·0429.	V. Pressure correction.	VI. T_j.	VII. $T_T - T_j$.	VIII. Δ.	IX. δ.
7·828	207·47	184·14	7·8996	−·0707	7·829	−·001		
9·375	243·51	220·17	9·4453	·0794	9·366	+·009		
12·293	311·89	288·56	12·3792	·0960	12·283	·010		
12·534	317·43	294·10	12·6169	·0973	12·520	·014		
13·127	331·32	307·99	13·2128	·1007	13·112	·015	+·020	+·005
13·310	335·40	312·07	13·3878	·1017	13·286	·024	·021	−·003
13·324	335·93	312·60	13·4105	·1018	13·309	·015	·021	+·006
13·737	345·23	321·90	13·8095	·1040	13·706	·031	·021	−·010
14·186	356·13	332·80	14·2771	·1067	14·170	·016	·021	+·005
15·416	385·01	361·68	15·5161	·1139	15·402	·014	·022	+·008
15·843	394·78	371·45	15·9352	·1163	15·819	·024	·023	−·001
18·291	451·83	428·50	18·3826	·1310	18·252	·039	·025	−·014
18·577	458·99	435·66	18·6898	·1329	18·557	·020	·025	+·005
18·699	461·57	438·24	18·8005	·1336	18·667	·032	·026	−·006
18·777	463·30	439·97	18·8747	·1340	18·741	·036	·026	−·010
21·145	519·38	496·05	21·2805	·1489	21·132	·013	·028	+·015
23·954	585·35	562·02	24·1106	·1164	23·944	·010		
24·761	604·20	580·87	24·9263	·1714	24·755	·006		
30·894	748·07	724·74	33·0913	·2105	30·881	·013		

the actual temperature on the French hard-glass mercury scale as determined by the Tonnelot. The second column gives the corresponding readings of "Joule A." As Joule, in his work, assumed a fixed zero of his thermometer, we must reduce the observations here also in the same way.

Any convenient position may be assumed as zero, as the scale-value which is to be deduced from the observations will only depend on the differences of readings, so that the zero is really eliminated. But it is convenient to take as zero that corresponding to the average temperature of the air, which in our case was about 23·33. The third column gives, therefore, the numbers obtained by subtracting 23·33 from the readings given in the second column. If Joule's scale-value is correct these figures should, when multiplied by his factor, give the temperature as determined by a thermometer made of glass having the composition of these thermometers. Joule's reducing factor is 0·077214, which for the Centigrade scale becomes ·042897. For convenience of calculation I have taken it as ·0429. The fourth column gives the numbers so reduced. Columns V. and VI. give the corrections to the vertical position and the corrected readings. The last column gives the differences between the temperatures as determined by the Tonnelot and Joule's thermometer respectively. These numbers show no very marked increase or diminution between the temperatures of 10° and 30°. If the numbers in column VI. were constant throughout, it would mean that the two thermometers read alike as regards differences of temperature.

In order to obtain the greatest possible information from the numbers obtained they were reduced by the method of least squares, all comparisons below 13° and above 22° being left out of account as lying outside the range within which Joule worked. If T_j represents the reading on the Joule thermometer, T_T that on the Tonnelot, and we wish to form an equation

$$T_T - T_j = a + bT_T$$

we may do so, substituting for $T_T - T_j$ the number in column VI., and for T_T those in column I. The constants a and b were thus found to be

$$a = 0·0081, \quad b = 0·000933 \pm ·00068.$$

If we denote by t_T and t_j *intervals* on the two thermometers we finally find

$$t_j = t_T\,(1 - 0·00093).$$

The result of this calculation, therefore, would be that the scale of the Joule thermometer is about one part in a thousand smaller than that of the Tónnelot, the difference being due either to a difference in the glass or to faulty calibration.

In order to compare the observed differences in the readings of the two thermometers with the values calculated from the most probable scale-value of the Joule, I have added columns VIII. and IX., the former giving the calculated value of $T_T - T_j$, and the latter the difference δ which is either due to errors of observation or to irregular errors of graduation of one or other of the thermometers. Although the obvious fault in this respect shown by the Joule prepares us for occasional differences of about 0°·01, I was not, for several reasons, satisfied with the results of this series of comparisons. The apparatus had not reached its final form during these experiments, the stirring was not as good, and the thermometer had not yet been protected against the inflow of cold water through the opening in the roof of the inner box. A great difficulty was also found in comparing together directly the Joule thermometer, which was rather sluggish in its motion, with the Tonnelot, which answered very quickly the smallest change of temperature. Unless care was taken, therefore, to make the rise exceedingly uniform errors were easily made. Additional uncertainty was introduced by the frequent redeterminations of the zero of the Tonnelot. The probable error of the calculated coefficient was too great to allow me to be satisfied with its value.

A second series of experiments was therefore decided upon, and as in a joint research in the equivalent of heat I had occasion, together with Mr. Gannon, to determine with considerable accuracy the scale-value of a Baudin thermometer graduated directly to a 50th of a degree, I made use of the latter in the second series.

The experiments were made exactly in the same way as before, the Joule being directly compared with the Baudin, and zero readings being dispensed with. The results are embodied in Table VI. The first column gives the temperatures according to the Joule thermometer, the coefficient ·0429 being again used, and the readings being converted to the vertical position. The second column gives the reading according to the Baudin thermometer, after the proper calibration correction had been applied and the reading also reduced to the vertical position. The third column gives the difference between the numbers in the two first.

TABLE VI.

I. T_j.	II. T_B.	III. T_B-T_j observed.	IV. T_B-T_j calculated.	V. δ.
13·9339	13·9452	+·0113	+·0111	−·0002
14·2114	14·2206	·0092	·0113	+·0021
14·4258	14·4359	·0101	·0115	+·0014
14·6885	14·7005	·0120	·0118	−·0002
14·9996	15·0120	·0124	·0121	−·0003
15·3201	15·3348	·0147	·0124	−·0023
15·7703	15·7866	·0163	·0128	−·0035
16·1221	16·1399	·0178	·0131	−·0047
16·5334	16·5413	·0079	·0135	+·0056
16·9247	16·9383	·0136	·0138	+·0002
17·2941	17·3103	·0162	·0142	−·0020
17·4847	17·4981	·0134	·0143	+·0009
17·7256	17·7380	·0124	·0146	+·0022
18·0034	18·0170	·0136	·0148	+·0012
18·2883	18·3015	·0132	·0151	+·0019
18·5526	18·5795	·0169	·0153	−·0016
18·7501	18·7660	·0159	·0155	−·0004
19·0095	19·0186	·0091	·0157	+·0066
19·2720	19·2907	·0187	·0160	−·0027
19·5116	19·5318	·0202	·0162	−·0040
19·7012	19·7174	·0162	·0164	+·0002
19·9254	19·9427	·0173	·0166	−·0007

The figures of this table were reduced in the same way as those of the first series of measurements. If we write

$$T_B - T_j = a + bT_B,$$

we find by the method of least squares

$$a = -\cdot 0017,$$

$$b = +\cdot 00092 \pm \cdot 00022.$$

The values of $T_B - T_j$ calculated by this formula are entered into the fourth column of Table VI. The differences δ between the calculated and observed values, which are also given, are seen to be as small as can be expected, never rising to more than 0°·006. This series having yielded a satisfactory comparison, we must reduce the scale-values obtained by applying the scale-correction of the Baudin thermometer. Denoting the intervals as read off by the thermometers by the small letter t, the above reductions give

$$t_j = t_B(1 - \cdot 00092).$$

A small correction is necessitated by the fact that a slight error was discovered in the pressure-coefficient of the Baudin thermometer after all the above reductions had been made. The corrected interval equation becomes

$$t_j = t_B(1 - \cdot 00084).$$

The comparison between the Baudin and Tonnelot thermometers made by Mr. Gannon and myself had given

$$t_T - t_B = -\cdot 00089 t_B.$$

Hence, by combining the last two equations,

$$t_j = t_T(1 + \cdot 00005).$$

This comparison would therefore show that the Joule and Tonnelot thermometers read exactly alike.

In all these measurements the Baudin and Joule were always read like calorimeter thermometers, without regard to the change of the freezing-point, while the Tonnelot was referred in every case to its proper zero. The equality of the scale-value of the two thermometers does not hold when they are both read in the same way, but the same interval read on the Tonnelot would be about one part in a thousand smaller than if read on A.

We may combine the results of the two series of comparisons by giving each weights inversely proportional to the probable error of the quantity denoted by b.

We therefore find as the most probable value for t_j,

$$t_j = t_T(1 - \cdot 00027).$$

Without attaching undue importance to this number, we may say that it represents the relation between the Tonnelot standard and Joule's thermometer as accurately as the divisions and calibration of the latter will allow us to judge. The number seems certainly not to be in error by more than one part in a thousand, and probably by less.

The transition to the nitrogen and hydrogen scale may now be made. Using Chappuis' experimental investigation on the French hard-glass thermometers, it is found that a temperature of 16°·5, to which Joule's last equivalent determination refers the interval on the Tonnelot thermometer, is to be diminished by ·00268 or ·00305 *, according as we want to obtain the interval on the nitrogen or hydrogen scale. Thus writing

$$t_N = t_T(1 - \cdot 00268),$$
$$t_H = t_T(1 - \cdot 00305),$$

we find

$$t_j = t_N(1 + \cdot 0024),$$
$$t_j = t_H(1 + \cdot 0028).$$

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* See Schuster and Gannon, Proc. Roy. Soc. lvii. p. 28

There is a marked difference between the results of this investigation and that deduced by Rowland [*] from the comparison of Joule's thermometers with his Baudin No. 6166. Tables VII. (referring to the first of the above series of comparisons) and VIII. (to the second) are intended to bring out this difference.

The numbers entered into the different columns of Table VII. are as follows:—

Column I. T_T or the reading on the Tonnelot thermometer.

„ II. $T_T - T_j$ or the corresponding difference in the reading on the scale used by Joule and the Tonnelot scale.

„ III. $T_N - T_T$, the correction to the Chappuis nitrogen-scale as interpolated between the numbers given in the table at the end of Guillaume's *Thermométrie.*

„ IV. The calculated difference $(T_j - T_N)$ between the Joule and Chappuis nitrogen-scale.

„ V. The corresponding difference $(T_j - T_N)_R$ between the Joule and Rowland's air-thermometers.

„ VI. The difference δ between the numbers given in Columns IV. and V.

A word of explanation is necessary as to how the numbers of Column V. have been obtained. Rowland gives in his paper the difference in the readings between Joule A and what he calls the "perfect" air-thermometer at a great number of points, none of them corresponding of course exactly to those of Column I., for which they are here required. I have taken the average between the value given for the temperature which lies nearest to that of Column I. and the two which lie immediately above and below it. The figures alter sufficiently slowly and with sufficient regularity to allow us to consider the numbers thus found as substantially correct.

We may deal more simply with the numbers obtained in the second series. The comparison between the Tonnelot and the Baudin thermometer already referred to gave, for the connexion between the two, the equation

$$T_T - T_B = {\cdot}0194 - {\cdot}00089\,T_B.$$

Combining with this the experimental connexion between the Joule and Baudin,

$$T_B - T_j = -{\cdot}0017 + {\cdot}00084\,T_B,$$

$$T_T - T_j = {\cdot}0177 - {\cdot}00005\,T_T;$$

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[*] Proc. Amer. Acad. xvi. p. 38.

and from this we may calculate for the temperatures lying between 14° and 22° the difference between the Tonnelot and Joule readings. These are entered in Column II. of Table VIII.; the remaining columns have the same meaning as those in Table VII.

TABLE VII.

I.	II.	III.	IV.	V.	VI.
T_T.	$T_T - T_j$.	$T_N - T_T$.	$T_j - T_N$.	$(T_j - T_N)_R$.	δ.
7·828	−·001	−·037	·038	·052	·014
9·375	+·009	·043	·034	·058	·024
12·293	·010	·054	·044	·077	·033
12·534	·014	·055	·041	·079	·038
13·127	·015	·056	·041	·080	·039
13·310	·024	·057	·033	·083	·050
13·324	·015	·057	·042	·083	·041
13·737	·031	·058	·027	·085	·058
14·186	·016	·059	·043	·085	·042
15·416	·014	·063	·049	·094	·045
15·843	·024	·064	·040	·094	·054
18·291	·039	·069	·030	·104	·074
18·577	·020	·072	·052	·104	·052
18·699	·032	·072	·040	·104	·064
18·777	·036	·070	·064	·104	·040
21·145	·013	·077	·064	·108	·044
23·954	·010	·083	·073	·112	·045
24·761	·006	·084	·078	·116	·038
30·894	·013	·092	·079		

TABLE VIII.

I.	II.	III.	IV.	V.	VI.
T_T.	$T_T - T_j$.	$T_N - T_T$.	$T_j - T_N$.	$(T_j - T_N)_R$.	δ.
12°	+·0171	−·053	·036	·077	·041
14	·0170	−·059	·042	·085	·043
16	·0169	−·065	·048	·094	·046
18	·0168	−·070	·054	·101	·047
20	·0167	−·075	·058	·109	·051
22	·0166	−·079	·062	·110	·048

The two series of measurements agree in showing a difference of nearly 0°·05, which must be either due to a real difference between Rowland's "perfect" air-thermometer and that of Chappuis, or to some error in one or other of the comparisons.

We have no information at all as to how Joule proceeded in comparing together his thermometer with that of Rowland. The numbers furnished by Joule are obviously not those obtained directly by experiment, as they are given to the thousandth part of a division. Joule probably only gave the mean between a certain number of successive observations ranging over several divisions of his scale. He would in this way eliminate the errors of division, and the regularity in the difference between his and Rowland's thermometer shows that some such process must have been adopted. There are certain corrections also no doubt applied by Joule, such as that due to the emergent stem, about which it would be necessary to have further information, before any definite conclusions can be drawn.

The important question as to a possible difference in the air-thermometers of Rowland and Chappuis can only be set at rest by a direct comparison of one of Rowland's thermometers with one compared at the Bureau International des Poids et Mesures.

But as regards the main point of the present investigation, this question does not arise. We are only concerned with Joule's thermometer, and the comparison between it and the Paris standard.

The relation between the intervals obtained by combining the two series of comparison was found to be, in terms of the Tonnelot nitrogen and hydrogen scales,

$$\begin{aligned} t_j &= t_T(1-\cdot00027) \\ &= t_N(1+\cdot0024) \\ &= t_H(1+\cdot0028). \end{aligned}$$

Joule's final value for the equivalent of heat therefore reduces as follows :—

Joule's value for a temperature 61°·69 F. (16°·5 C.).	772·65
On the scale of the French hard-glass thermometer.	772·44
On the scale of the nitrogen thermometer of the Bureau International des Poids et Mesures . .	774·51
On the scale of the hydrogen thermometer of the Bureau International des Poids et Mesures . . .	774·81

Rowland applies a small correction to Joule's value of the heat-capacity of his calorimeter. This would raise the equivalent by ·2. Taking account of this, and considering that Joule's thermometer was never intended to measure temperatures nearer than one part in a thousand, and is not graduated sufficiently well to allow the decimal place to be determined with any certainty, we may state it as the result of this investigation that

Joule's equivalent of heat resulting from his own investigations *and reduced to the nitrogen thermometer of the Bureau International des Poids et Mesures is to the nearest unit* 775 *foot-pounds at the sea-level and the latitude of Greenwich.* The number refers to a pound of water weighed *in vacuo* at a temperature of 61°·7 F. (16°·5 C.).

The equivalent reduced to ergs becomes $4{\cdot}173 \times 10^{-7}$.

It is not necessary to discuss the older observations of Joule, or to modify his numbers by attaching weights to his experiments different from those which he gave to them himself. The result of Joule's last paper, as reduced by himself, should be taken as his final judgment. Rowland's value at 16°·5 is $4{\cdot}186 \times 10^{7}$, but the results of this paper open out the possibility that this number might have to be reduced somewhat when referred to the Paris air-thermometer. It seems most probable that the correct value of the equivalent lies somewhere between Joule's value and that of Rowland. The higher values obtained by Mr. Griffiths and myself and Gannon by the electrical method are not easily accounted for, but for the present they cannot in my opinion be put into competition with the direct determinations of Joule and Rowland. The discrepancy no doubt will be cleared up. In the meantime a comparison between one of Rowland's thermometers and the Paris standard would be of great interest.

XLIX. *On the Kinetic Energy of the Motion of Heat and the corresponding Dissipation Function. By* Dr. LADISLAS NATANSON, *Professor of Natural Philosophy, University of Cracow*[*].

1. IN the following the fundamental assumptions of the former paper ("On the Kinetic Interpretation of the Dissipation Function") will be adopted. A fluid medium is considered which is supposed to consist of a multitude of moving molecules. Let u, v, w be the components of the "molar" velocity, *i. e.* of the mean velocity of the molecules within an element $dx\,dy\,dz$; and let ξ, η, ζ be the components of the individual velocity of any given molecule in that element. We will employ the symbol ρ to denote the density of the medium; and Q to denote any property of a molecule which depends on the values of $(u+\xi)$, $(v+\eta)$, and $(w+\zeta)$. Let $\overline{Q}$ indicate the mean value of Q for all molecules within

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an element, and X, Y, Z the components of acceleration due to external forces at the point (x, y, z). We will write $d\overline{Q}/dt$ the total or actual variation of $\overline{Q}$; and by $\delta\overline{Q}/\delta t$ we will represent such variation of $\overline{Q}$ as can be due to the mutual interference between molecules. Then (Maxwell, "On the Dynamical Theory of Gases," Scientific Papers, ii. p. 26),

$$\rho\frac{d\overline{Q}}{dt}+\frac{\partial}{\partial x}(\overline{\xi Q\rho})+\frac{\partial}{\partial y}(\overline{\eta Q\rho})+\frac{\partial}{\partial z}(\overline{\zeta Q\rho})$$

$$=\rho\frac{\delta\overline{Q}}{\delta t}+\rho X\frac{\partial\overline{Q}}{\partial u}+\rho Y\frac{\partial\overline{Q}}{\partial v}+\rho Z\frac{\partial\overline{Q}}{\partial w}. \quad . \quad (1)$$

If we give to Q in this equation consecutively such significations as are consistent with definition and then eliminate terms including X, Y, Z and $\delta/\delta t$, a set of propositions will be obtained, constituting what may be called a *Kinematical* Theory of Fluids, a theory of rather high degree of generality which must not be confounded with special molecular theories of usually very hypothetical character. It is with Hydrodynamics that the kinematical theory seems to be most intimately connected, the fundamental hydrodynamical equations (or possibly some generalizations thereof) being simple deductions from the equations of that theory.

2. In equation (1) put

$$Q=(u+\xi)\{(u+\xi)^2+(v+\eta)^2+(w+\zeta)^2\}; \quad . \quad . \quad (2)$$

and let us write for brevity,

$$\overline{\xi(\xi^2+\eta^2+\zeta^2)}=r_x. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Neglecting small terms we obtain

$$\rho\frac{d}{dt}\{u(u^2+v^2+w^2)+u(3\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})+r_x\}$$

$$+\frac{\partial}{\partial x}\{\rho\overline{\xi^2}(3u^2+v^2+w^2)+\rho\overline{\xi^2(\xi^2+\eta^2+\zeta^2)}\}$$

$$+\frac{\partial}{\partial y}(2uv\rho\overline{\eta^2})+\frac{\partial}{\partial z}(2uw\rho\overline{\zeta^2})=2\rho u\frac{\delta\overline{\xi^2}}{\delta t}+\rho\frac{\delta r_x}{\delta t}$$

$$+\rho X(3u^2+v^2+w^2+3\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})+2\rho Yuv+2\rho Zuw. \quad (4)$$

We shall simplify this equation, being satisfied with a first approximation. Put in (1) $Q=(u+\xi)^2$; put, again, $Q=u+\xi$, multiply by $2u$, and to a first approximation it follows,

$$2\rho\frac{d\overline{\xi^2}}{dt}+4\rho\overline{\xi^2}\frac{\partial u}{\partial x}=2\rho\frac{\delta\overline{\xi^2}}{\delta t}. \quad . \quad . \quad . \quad . \quad (5)$$

Similarly equation (11) of the former paper becomes here

$$\rho\frac{d}{dt}(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})+2\rho\overline{\xi^2}\frac{\partial u}{\partial x}+2\rho\overline{\eta^2}\frac{\partial v}{\partial y}+2\rho\overline{\zeta^2}\frac{\partial w}{\partial z}=0. \qquad (6)$$

From (5), (6), and from (8) in the former paper we obtain

$$\rho\frac{d}{dt}\{u(u^2+v^2+w^2)+u(3\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\}+6\rho\overline{\xi^2}u\frac{\partial u}{\partial x}+2\rho\overline{\eta^2}u\frac{\partial v}{\partial y}+2\rho\overline{\zeta^2}u\frac{\partial w}{\partial z}$$

$$+(3u^2+v^2+w^2+3\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\frac{\partial}{\partial x}(\rho\overline{\xi^2})+2uv\frac{\partial}{\partial y}(\rho\overline{\eta^2})+2uw\frac{\partial}{\partial z}(\rho\overline{\zeta^2})$$

$$=2\rho u\frac{\delta\overline{\xi^2}}{\delta t}+(3u^2+v^2+w^2+3\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\rho X+2uv\rho Y+2uw\rho Z, \quad . \ (7)$$

whence, comparing with (4),

$$\rho\frac{dr_x}{dt}+\frac{\partial}{\partial x}(\rho\overline{\xi^2(\xi^2+\eta^2+\zeta^2)})-(3\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\frac{\partial}{\partial x}(\rho\overline{\xi^2})$$

$$+2v\left(\rho\overline{\xi^2}\frac{\partial v}{\partial x}+\rho\overline{\eta^2}\frac{\partial u}{\partial y}\right)+2w\left(\rho\overline{\xi^2}\frac{\partial w}{\partial x}+\rho\overline{\zeta^2}\frac{\partial u}{\partial z}\right)=\rho\frac{\delta r_x}{\delta t}. \qquad (8)$$

If the disturbance is not a very violent one, the first, the fourth, and the fifth member on the left-hand side may be omitted. Hence

$$\rho\frac{\delta r_x}{\delta t}=\frac{\partial}{\partial x}(\rho\overline{\xi^2(\xi^2+\eta^2+\zeta^2)})-(3\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\frac{\partial}{\partial x}(\rho\overline{\xi^2}), \qquad (9)$$

an equation which (under somewhat particular assumptions) was given by Maxwell. Let us write

$$D_x=\overline{\xi^2(\xi^2+\eta^2+\zeta^2)}-\overline{\xi^2}\,.\,(3\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\ ; \quad . \ . \ . \ (10)$$

equation (9) becomes

$$\rho\frac{\delta r_x}{\delta t}=\frac{\partial}{\partial x}(\rho D_x)+\rho\overline{\xi^2}\frac{\partial}{\partial x}(3\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2}). \quad . \ (11)$$

Now this equation would lead at once to results contrary to experience, as shown by Maxwell, unless $D_x=0$; accordingly the first term on the right-hand side may be dropped. And if $\overline{\xi^2}$, $\overline{\eta^2}$, and $\overline{\zeta^2}$ can be replaced each with sufficient approximation by $\frac{1}{3}(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})$, we shall have

$$\rho\frac{\delta r_x}{\delta t}=\frac{5}{3}\rho\overline{\xi^2}\frac{\partial}{\partial x}(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2}), \quad . \ . \ . \ (12)$$

an approximate equation which is of secondary importance only in the subsequent calculation.

3. Let us now proceed to prove our principal equation.

Putting in (1) $Q=(u+\xi)^2$ and again $Q=u+\xi$ and multiplying by $2u$ we obtain (without neglecting any term)

$$\rho\frac{d\overline{\xi^2}}{dt}+2\rho\overline{\xi^2}\frac{\partial u}{\partial x}+2\rho\overline{\xi\eta}\frac{\partial u}{\partial y}+2\rho\overline{\xi\zeta}\frac{\partial u}{\partial z}$$

$$+\frac{\partial}{\partial x}(\rho\overline{\xi^3})+\frac{\partial}{\partial y}(\rho\overline{\eta\xi^2})+\frac{\partial}{\partial z}(\rho\overline{\zeta\xi^2})=\rho\frac{\delta\overline{\xi^2}}{\delta t}. \quad . \quad (13)$$

Again, let

$$\Psi=\rho\overline{\xi^2}\frac{\partial u}{\partial x}+\rho\overline{\eta^2}\frac{\partial v}{\partial y}+\rho\overline{\zeta^2}\frac{\partial w}{\partial z}$$

$$+\rho\overline{\eta\zeta}\left(\frac{\partial v}{\partial z}+\frac{\partial w}{\partial y}\right)+\rho\overline{\zeta\xi}\left(\frac{\partial w}{\partial x}+\frac{\partial u}{\partial z}\right)+\rho\overline{\xi\eta}\left(\frac{\partial u}{\partial y}+\frac{\partial v}{\partial x}\right)(14)$$

and

$$r_y=\overline{\eta(\xi^2+\eta^2+\zeta^2)}, \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$r_z=\overline{\zeta(\xi^2+\eta^2+\zeta^2)}. \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Then

$$\rho\frac{d}{dt}(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})+2\Psi+\frac{\partial\rho r_x}{\partial x}+\frac{\partial\rho r_y}{\partial y}+\frac{\partial\rho r_z}{\partial z}=0. \quad . \quad (17)$$

Assuming $D_x=0$:

$$\frac{d}{dt}(\overline{\xi^2(\xi^2+\eta^2+\zeta^2)})=(5\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\frac{d\overline{\xi^2}}{dt}+\overline{\xi^2}\frac{d}{dt}(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2}); \quad (18)$$

whence, by (13) and (17),

$$\rho\frac{d}{dt}(\overline{\xi^2(\xi^2+\eta^2+\zeta^2)})=$$

$$-2\overline{\xi^2}\Psi-\overline{\xi^2}\left(\frac{\partial\rho r_x}{\partial x}+\frac{\partial\rho r_y}{\partial y}+\frac{\partial\rho r_z}{\partial z}\right)+(5\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\rho\frac{\delta\overline{\xi^2}}{\delta t}$$

$$-(5\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\left(2\rho\overline{\xi^2}\frac{\partial u}{\partial x}+2\rho\overline{\xi\eta}\frac{\partial u}{\partial y}+2\rho\overline{\xi\zeta}\frac{\partial u}{\partial z}\right)$$

$$-(5\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\left(\frac{\partial}{\partial x}(\rho\overline{\xi^3})+\frac{\partial}{\partial y}(\rho\overline{\eta\xi^2})+\frac{\partial}{\partial z}(\rho\overline{\zeta\xi^2})\right). \quad (19)$$

From this and similar equations we have

$$\rho\frac{d}{dt}(\overline{(\xi^2+\eta^2+\zeta^2)^2})=-2(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\Psi$$

$$-(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\left(\frac{\partial\rho r_x}{\partial x}+\frac{\partial\rho r_y}{\partial y}+\frac{\partial\rho r_z}{\partial z}\right)+L-2M-N, \quad (20)$$

the symbols L, M, N being defined as follows :—

$$\mathrm{L}=\rho\left\{(5\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\frac{\delta\overline{\xi^2}}{\delta t}+(\overline{\xi^2}+5\overline{\eta^2}+\overline{\zeta^2})\frac{\delta\overline{\eta^2}}{\delta t}+(\overline{\xi^2}+\overline{\eta^2}+5\overline{\zeta^2})\frac{\delta\overline{\zeta^2}}{\delta t}\right\}. \quad (21)$$

$$\begin{aligned}\mathrm{M}=&(5\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\left(\rho\overline{\xi^2}\frac{\partial u}{\partial x}+\rho\overline{\xi\eta}\frac{\partial u}{\partial y}+\rho\overline{\xi\zeta}\frac{\partial u}{\partial z}\right)\\&+(\overline{\xi^2}+5\overline{\eta^2}+\overline{\zeta^2})\left(\rho\overline{\eta\xi}\frac{\partial v}{\partial x}+\rho\overline{\eta^2}\frac{\partial v}{\partial y}+\rho\overline{\eta\zeta}\frac{\partial v}{\partial z}\right)\\&+(\overline{\xi^2}+\overline{\eta^2}+5\overline{\zeta^2})\left(\rho\overline{\zeta\xi}\frac{\partial w}{\partial x}+\rho\overline{\zeta\eta}\frac{\partial w}{\partial y}+\rho\overline{\zeta^2}\frac{\partial w}{\partial z}\right). \quad . \quad . \quad . \quad (22)\end{aligned}$$

$$\begin{aligned}\mathrm{N}=&(5\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\left(\frac{\partial}{\partial x}(\rho\overline{\xi^3})+\frac{\partial}{\partial y}(\rho\overline{\eta\xi^2})+\frac{\partial}{\partial z}(\rho\overline{\zeta\xi^2})\right)\\&+(\overline{\xi^2}+5\overline{\eta^2}+\overline{\zeta^2})\left(\frac{\partial}{\partial x}(\rho\overline{\xi\eta^2})+\frac{\partial}{\partial y}(\rho\overline{\eta^3})+\frac{\partial}{\partial z}(\rho\overline{\zeta\eta^2})\right)\\&+(\overline{\xi^2}+\overline{\eta^2}+5\overline{\zeta^2})\left(\frac{\partial}{\partial x}(\rho\overline{\xi\zeta^2})+\frac{\partial}{\partial y}(\rho\overline{\eta\zeta^2})+\frac{\partial}{\partial z}(\rho\overline{\zeta^3})\right). \quad . \quad (23)\end{aligned}$$

We easily find, to a first approximation, L=0, and

$$\mathrm{M}=\tfrac{7}{3}(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\Psi, \quad . \quad . \quad . \quad . \quad . \quad (24)$$

$$\mathrm{N}=\tfrac{7}{3}(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\left(\frac{\partial\rho r_x}{\partial x}+\frac{\partial\rho r_y}{\partial y}+\frac{\partial\rho r_z}{\partial z}\right); \quad . \quad (25)$$

thus equation (20) becomes

$$\begin{aligned}&\rho\frac{d}{dt}(\overline{(\xi^2+\eta^2+\zeta^2)^2})\\&=-\tfrac{20}{3}(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\Psi-\tfrac{10}{3}(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\left(\frac{\partial\rho r_x}{\partial x}+\frac{\partial\rho r_y}{\partial y}+\frac{\partial\rho r_z}{\partial z}\right). \quad (26)\end{aligned}$$

To the left-hand side let us add

$$\overline{(\xi^2+\eta^2+\zeta^2)^2}\left\{\frac{d\rho}{dt}+\rho\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}\right)\right\}; \quad . \quad (27)$$

calling

$$\tfrac{1}{4}\rho(\overline{\xi^2+\eta^2+\zeta^2)^2}=\mathrm{A}, \quad . \quad . \quad . \quad . \quad . \quad (28)$$

we obtain

$$\begin{aligned}&\frac{\partial\mathrm{A}}{\partial t}+\frac{\partial}{\partial x}(u\mathrm{A})+\frac{\partial}{\partial y}(v\mathrm{A})+\frac{\partial}{\partial z}(w\mathrm{A})\\&\qquad=-\tfrac{5}{3}(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\Psi-\tfrac{5}{6}(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\left(\frac{\partial\rho r_x}{\partial x}+\frac{\partial\rho r_y}{\partial y}+\frac{\partial\rho r_z}{\partial z}\right). \quad (29)\end{aligned}$$

If we make $3p=\rho(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})$ and introduce Lord Rayleigh's

Dissipation Function F defined as follows :—

$$\mathrm{F}=(p-\rho\overline{\xi^2})\frac{\partial u}{\partial x}+(p-\rho\overline{\eta^2})\frac{\partial v}{\partial y}+(p-\rho\overline{\zeta^2})\frac{\partial w}{\partial z}$$
$$-\rho\overline{\eta\zeta}\left(\frac{\partial v}{\partial z}+\frac{\partial w}{\partial y}\right)-\rho\overline{\zeta\xi}\left(\frac{\partial w}{\partial x}+\frac{\partial u}{\partial z}\right)-\rho\overline{\xi\eta}\left(\frac{\partial u}{\partial y}+\frac{\partial v}{\partial x}\right), \quad (30)$$

we shall have

$$\Psi=-\mathrm{F}+p\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}\right). \quad . \quad . \quad . \quad (31)$$

Returning to (29), multiplying by $dx\,dy\,dz$ and integrating throughout the volume occupied by the medium,

$$\frac{\partial}{\partial t}\iiint \mathrm{A}\,dx\,dy\,dz=-\iint \mathrm{A}(lu+mv+nw)\,d\mathrm{S}$$
$$+\tfrac{5}{3}\iiint(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\mathrm{F}\,dx\,dy\,dz-\tfrac{5}{3}\iiint(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})p\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}\right)dx\,dy\,dz$$
$$-\tfrac{5}{6}\iiint\rho(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})(lr_x+mr_y+nr_z)d\mathrm{S}$$
$$+\tfrac{5}{6}\iiint\left\{\rho r_x\frac{\partial}{\partial x}(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})+\rho r_y\frac{\partial}{\partial y}(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\right.$$
$$\left.+\rho r_z\frac{\partial}{\partial z}(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\right\}dx\,dy\,dz. \quad (32)$$

Here the direction-cosines of the normal to the element $d\mathrm{S}$ of the surface are denoted by l, m, n.

4. In order to interpret equation (32) let us adopt a somewhat generalized definition of "Kinetic Energy." Suppose **C** (a vector) to represent any current or *flux*, and let **q** be its velocity. We define then the kinetic energy per unit volume to be the scalar product

$$\tfrac{1}{2}\mathrm{S}(\mathbf{Cq})=\tfrac{1}{2}(\mathrm{C}'q'+\mathrm{C}''q''+\mathrm{C}'''q'''), \quad . \quad . \quad . \quad (33)$$

C', C'', and C''' being the components of **C**, and q', q'', and q''' the components of **q**. Thus, if **C** means an ordinary flux of matter, of density ρ, then $\mathbf{C}=\rho\mathbf{q}$, and the "kinetic energy" of matter, *i.e.* the kinetic energy in the case of a matter-flux, is found as usually given. But we are now enabled to form an idea of "kinetic energy" in other cases as well. Thus in the case we are dealing with, the motion of a molecule through space may be said to be equivalent to a "*molecular current*" of the quantity Q carried about by the molecule; and then $\xi\mathrm{Q}$, $\eta\mathrm{Q}$, and $\zeta\mathrm{Q}$ will be the values of the components of that current. From (33) we conclude that the kinetic energy of such a molecular current of Q is

$$\tfrac{1}{2}(\xi^2+\eta^2+\zeta^2)\mathrm{Q}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

and the total kinetic energy of such currents per unit volume is

$$\tfrac{1}{2}\mathrm{N}(\overline{(\xi^2+\eta^2+\zeta^2)\mathrm{Q}}), \quad . \quad . \quad . \quad . \quad . \quad (35)$$

N being the number of molecules per unit volume. Calling now M the mass of a molecule, let us consider the flux of the quantity $\mathrm{Q}=\frac{1}{2}\mathrm{M}(\xi^2+\eta^2+\zeta^2)$: we see that (35) becomes equal to A as defined by (28); A therefore represents the total kinetic energy of molecular currents of (ordinary) molecular energy in unit volume, *i. e.* the kinetic energy of the motion of heat-energy in unit volume, and $\iiint \mathrm{A}\,dx\,dy\,dz$ represents the same quantity for the total fluid. The idea of "*molecular currents*" is likely to conserve a definite meaning even when the idea of "molecules" will be found to be superseded.

5. The energy of motion of the heat-energy is susceptible of several kinds of variation, from various sources, to which the consecutive terms of the right-hand side of (32) refer. The first term represents the loss by convection across the surface; the second the gain due to viscosity; the third expresses the reversible effect of the mean pressure doing work. The fourth term relates to the communication of heat through the surface, since $\frac{1}{2}\rho r_x$, $\frac{1}{2}\rho r_y$, and $\frac{1}{2}\rho r_z$ are the values of the total component fluxes of energy. In order to find the meaning of the fifth term, let us substitute for the differential coefficients values from (12) and two other equations which can be written down from symmetry; then that term will be

$$\frac{1}{4}\iiint\left[\frac{1}{\rho\overline{\xi^2}}\cdot\frac{\delta}{\delta t}((\rho r_x)^2)+\frac{1}{\rho\overline{\eta^2}}\cdot\frac{\delta}{\delta t}((\rho r_y)^2)+\frac{1}{\rho\overline{\zeta^2}}\cdot\frac{\delta}{\delta t}((\rho r_z)^2)\right]dx\,dy\,dz, \quad (36)$$

and represents therefore the source of variation due to interaction between molecules. This we shall call the "interior" source of variation, whereas the foregoing will be described as "exterior" sources: in fact the "interior" source remains active even in a fluid at rest when contained in a surface impermeable to heat. We now see that the direction of the interior variation depends on the nature of the mutual action between molecules. Since the quantities $(\rho r_x)^2$, $(\rho r_y)^2$, and $(\rho r_z)^2$ are positive, the energy of the motion of heat-energy will be always decreasing if molecular interaction is such as to tend to diminish the absolute values of ρr_x, ρr_y, and ρr_z; in the opposite case that energy will be always increasing. That it is the first case only that is realized in all fluids in Nature, as attested by the phenomenon of conduction of heat, cannot be deduced from Kinematical Theory. We have ascertained, as it were, the path of change of the energy of the motion of heat-energy, but we are unable to say why one of the two possible directions of change is invariably selected.

6. It may be well to point out that the problem here discussed bears distinct analogy to the problem of our former paper, where the Dissipation Function F represented what may now be called the "interior" variation of molar fluid-energy and was seen to depend on the effect of molecular interaction on the values of

$$q_x=\rho\overline{\xi^2}-p \quad \text{and} \quad s_x=\rho\overline{\eta\zeta}, \quad . \quad . \quad . \quad . \quad (37)$$

and similar quantities, in analogy to the present proposition concerning the fifth term of (32), right-hand side. Put

$$\mu_x=-\frac{p\cdot q_x}{\frac{\delta q_x}{\delta t}}; \quad \nu_x=-\frac{p\cdot s_x}{\frac{\delta s_x}{\delta t}}, \quad . \quad . \quad . \quad . \quad (38)$$

and let μ_y, μ_z, ν_y, ν_z be defined by similar equations. Suppose the Kinematical Theory of the Viscosity-problem to be given; then what we have to do in order to complete the solution is simply to prove that the μ's and the ν's have constant and equal values: the results indeed given at the end of § 2 of the former paper, and likewise the well-known equations of motion of viscous fluids, can then be easily deduced. The common value of the μ's and the ν's is the coefficient of viscosity and is positive if the mutual action between molecules is such as to tend always to dissipate the disturbances q and s. Again, put

$$k_x=-\frac{5\rho\overline{\xi^2}r_x}{\frac{\delta r_x}{\delta t}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

and let k_y and k_z be defined by similar equations. It follows from (12) and (39) that

$$\rho r_x=-\tfrac{1}{3}k_z\frac{\partial}{\partial x}(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2}). \quad . \quad . \quad . \quad (40)$$

From (17) therefore we obtain, calling $\frac{1}{3}(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})=\theta$,

$$3\rho\frac{d\theta}{dt}+2\Psi-\left(\frac{\partial}{\partial x}\left(k_x\frac{\partial\theta}{\partial x}\right)+\frac{\partial}{\partial y}\left(k_y\frac{\partial\theta}{\partial y}\right)+\frac{\partial}{\partial z}\left(k_z\frac{\partial\theta}{\partial z}\right)\right)=0, (41)$$

the equation of conduction, as usually given, following from this for a fluid at rest, if it is conceded that θ means the temperature at (xyz). The value of the last term of equation (32) is now

$$-\frac{5}{6}\iiint\left\{k_x\left(\frac{\partial\theta}{\partial x}\right)^2+k_y\left(\frac{\partial\theta}{\partial y}\right)^2+k_z\left(\frac{\partial\theta}{\partial z}\right)^2\right\}dx\,dy\,dz. \quad . \quad (42)$$

In order to complete our solution we have to prove that the k's have constant and equal values. It will be observed that the *rôle* of the expression

$$\frac{5}{6}k\left\{\left(\frac{\partial\theta}{\partial x}\right)^2+\left(\frac{\partial\theta}{\partial y}\right)^2+\left(\frac{\partial\theta}{\partial z}\right)^2\right\} \quad . \quad . \quad (43)$$

in Conduction is much the same as that played by Lord Rayleigh's Dissipation Function F in Viscosity; and we therefore propose to call this expression "the Dissipation Function of Conduction."

In his great paper "On the Dynamical Theory of Gases," Maxwell practically confined himself to the case of a force between molecules varying inversely as the fifth power of their distance. It may, we think, be legitimately assumed that the Theory of Matter will progress in the future without the aid of any such hypothesis. Whatever may be the law of molecular force, whatever may even be the opinion we hold as to the existence of molecules, we shall be justified in seeking to find a *general law of subsidence of disturbances* in fluids or possibly in all bodies—a general *Law of Relaxation* in Maxwell's sense of the term. Let α, β, γ denote constants, being the reciprocals of time-periods; we have

$$\frac{\delta q_x}{\delta t}=-\alpha q_x;\quad \frac{\delta s_x}{\delta t}=-\gamma s_x;\quad \frac{\delta r_x}{\delta t}=-\beta r_x;\quad . \quad . \quad (44)$$

and it does not seem unlikely that these equations should be special and no doubt approximate expressions of some general relation.

The subsidence of disturbances, to which we alluded, forms a characteristic feature of phenomena which are going on in matter, as contrasted with those of which the æther is the seat. Now this property of gradually calming every kind of disturbance (which seems to be a fundamental property of matter) is in formal contrast with another property attributed to matter, *i. e.* with *inertia*. It seems therefore legitimate to suppose that it is with the properties of the æther that we are ultimately concerned in ordinary dynamics; and if we adopt the well-known doctrine which asserts that matter may consist in some kind of disturbance in the æther, we shall find nothing to surprise us in such an assumption.

L. *The Heat of Combination of Substances in the Liquid and Solid Condition.* By SPENCER UMFREVILLE PICKERING *F.R.S.*[*]

IF it were found that the heat of formation of a solid hydrate, or analogous compound, from its solid constituents were the same as that evolved when these constituents were mixed in the liquid condition, we should have a strong argument in favour of the view that the same substance was formed in the two cases—that the liquid mixture, just as much as the solid hydrate, consisted of a definite compound. The only instance in which sufficient data exist for the calculation of the heat of formation in the two conditions gives results indicating that this may be the case: taking the author's values for the monohydrate of sulphuric acid, it is found that solid water and solid sulphuric acid in combining to form the solid monohydrate evolve 6533 cal. at 17°·9, whereas the liquid constituents in combining to form the liquid hydrated acid at the same temperature evolve 6667 cal., practically the same amount of heat.

The present determinations were made in order to see whether a similar equality held good in other cases. The results obtained, however, have been of an entirely negative character, and show that the equality found in the case of sulphuric acid is, probably, accidental.

Negative results, however, do not in any way prove that the mixed liquids do not contain, or consist of, the compound known in the solid condition, for the actions concerned are complex, and the quantity which is measured as the heat of combination represents, in reality, the difference between this quantity and several others.

Thus, suppose, for the sake of argument, that the same amount of combination occurs when the substances are brought together in either of the two conditions: and let C represent the heat of combination of the molecules a and b to form ab. Then we have, when the substances are all liquids, the splitting up of the liquid aggregates into the molecules a and b, v_a and v_b, and the aggregation of the molecules of the compound into the liquid condition, so that the heat measured on mixing the liquids will be

$$H = C - v_a - v_b + v_{ab}.$$

When the substances are in the solid condition, we shall have similarly the heats of conversion of the *solids* into the molecular condition, or, since the action may be regarded as taking place in the two stages, we shall have, first, the conversion of the solids into the liquids (heat of fusion $=f$), and subsequently the conversion of these liquids into the molecular condition; the heat measured in this case will be

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[*] Communicated by the Author.

$$H'=C-v_a-v_b+v_{ab}-f_a-f_b+f_{ab}.$$

H will be equal to H′ only if $f_a+f_b=f_{ab}$; *i. e.* if the heat of fusion of the compound is equal to the sum of those of its constituents.

The fact that with hydrates and analogous compounds the chemical combination is of a comparatively feeble character rendered it not improbable that this might be the case; but there is no reason why it should necessarily be so, and the question can only be settled by direct experiment.

The present determinations show that it is not so. The above argument, as has been said, applies to a case where the amount of combination is supposed to be as great in the liquid as in the solid condition,—that is, where the heat of fusion of the compound, f_{ab}, represents nothing but the mere change from the solid to the liquid condition (true heat of fusion). If, however, the compound undergoes partial dissociation on fusion, this dissociation will (generally) involve absorption of heat, and its apparent heat of fusion will be greater than its true heat of fusion. The present determinations, however, show that the observed heat of fusion of the compound is generally *smaller* than the sum of those of its constituents, and, *a fortiori*, the true heat of fusion of the compound must be smaller still; therefore, the assumption that $f_a+f_b=f_{ab}$ is untenable, and no conclusions can be drawn as to the amount of dissociation occurring on melting the compound from the measurement of H and H′.

The heat of combination of two substances in the liquid condition was determined by dissolving each of them, and also the compound, separately in a solvent. D being the heat of dissolution, the heat of combination is

$$D_a+D_b-D_{ab}.$$

When, as was generally the case, one of the constituents (say a) was identical with the solvent, $D_a=0$.

With solids similar determinations were made; and where the solvent is identical with one of the reagents, D_a is the heat of fusion of the substance a.

As it was not possible to make the determinations in both conditions directly with each substance, the heat of dissolution in the one condition had to be calculated from that observed in the other by means of the heat of fusion. The heats of fusion of the substances had therefore to be determined, and to reduce these to the temperature used in the heats of dissolution determinations, the heat-capacity both in the liquid and solid conditions had also to be determined. A description of the method used and of the calculations will be found in the Proc. Roy. Soc. xlix. p. 11: it will be sufficient to state here that the substance is heated in a platinum bottle containing a thermometer to the required temperature, and then plunged into the calorimeter.

Table I. of the present communication gives the experimental details and Table II. the results. Table III. gives the values for the heat of dissolution—firstly, those obtained by direct experiment on the substance in the one condition, and, secondly, those calculated for it in the other condition, as deduced from the former by means of the heat of fusion.

The heat-capacity is calculated from the equation

$$C = \frac{(t'-t)W - (\tau - t')w'}{(\tau - t')w},$$

and the molecular heat of dissolution from the equation

$$D_m = \frac{(t'-t)WM}{w};$$

where t' and t are the final and initial temperatures of the calorimeter, W the water-equivalent of the calorimeter and its contents, τ the initial temperature of the substance when introduced into the calorimeter, w its weight, and M its molecular weight, w' being the water-equivalent of the platinum bottle containing it.

Considerable difficulty was experienced in finding substances suitable for the present investigation. In order that the heat of fusion may be satisfactorily determined, it is necessary that the compound and both of its constituents should melt between temperatures of 0° and not much above 100°. Several substances other than those here mentioned were examined and found unsuitable.

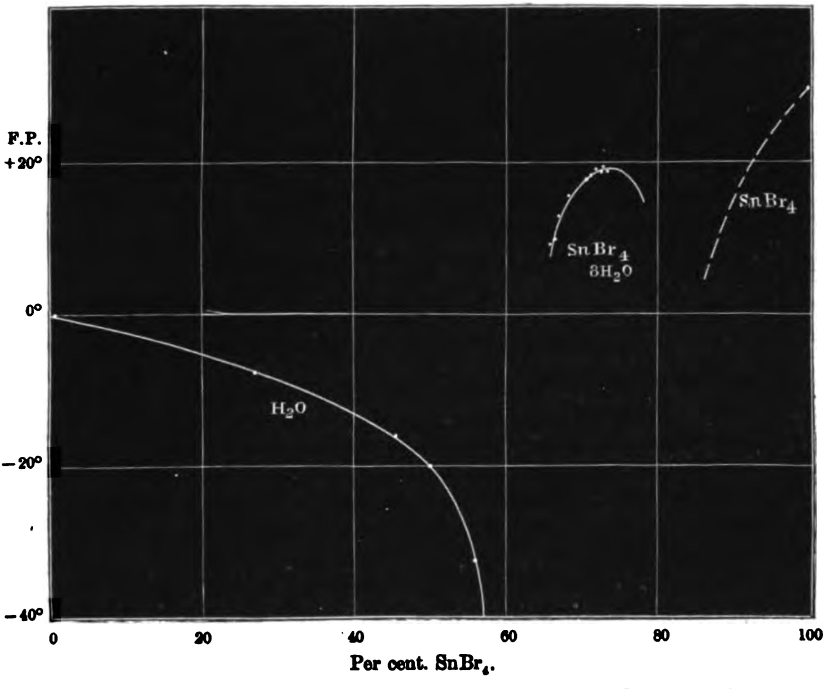
Monohydrate of Sulphuric Acid.—The necessary data have already been given in the Trans. Chem. Soc. 1890, p. 112, and the Proc. Roy. Soc. xlix. p. 18: a very slight alteration in them has been made in consequence of round values for the atomic weights having been used in the present work.

Hexhydrate of Pinacone.—To prepare the anhydrous from the hydrated pinacone supplied by Messrs. Kahlbaum, fractional distillation was found to be unsatisfactory, and dehydration by treatment of the ethereal solution with potassium carbonate was adopted. The hydrated substance does not appear to be by any means insoluble in ether, as is stated, and indeed it is improbable that any hydrate would be insoluble in a liquid which dissolves both the anhydrous substance and water. The melting-points of the anhydrous and hydrated substance were 40°·48 and 45°·42 respectively: Linnemann gives 35°–38° and 46°·5.

Anhydrous pinacone superfuses considerably, and in the case of the experiments Nos. 32 and 33, in which the liquid substance was taken at an initial temperature of 44°, it did not solidify till after it had attained the temperature of the calorimeter: the heat evolved when it did solidify was noted separately, and gave the two supplementary measurements entered in the footnote to Table II.

Octohydrate of Tin Tetrabromide.—The tetrachloride of tin forms a tetrahydrate; but as the anhydrous substance was found not to solidify till −34°·15, it was not a suitable substance for the present investigation. The tetrabromide, which solidifies at the higher temperature of 29°·36, was

Fig. 1.—Freezing-points of $SnBr_4$ solutions.



therefore examined in order to ascertain whether it also formed a hydrate. The results of a series of freezing-points of mixtures of it with water are given in Table IV. and fig. 1.

The freezing-point of the tetrabromide is no doubt lowered by the addition of water, and probably very rapidly so, for with 2½ per cent. of added water no crystallization was obtained at −70°; but with this amount of water, and also with amounts up to 24 per cent., mutual solution is not complete, the liquids being always cloudy. When the water is increased to about 26 per cent., the liquid is clear at high temperatures, and generally becomes cloudy on cooling (it did not do so in the experiment at 73·4 p.c. $SnBr_4$); and the more the added water is increased the lower is the temperature which the solution will stand without becoming cloudy. Hard, well-defined, transparent crystals were obtained from solutions containing 73·6 to 66·7 per cent. of the tetrabromide; but with the strongest of these solutions the liquid was turbid when solidification occurred, and the observations were difficult and doubtful. From solutions containing less than 56 per cent. of the bromide, water crystallizes. On plotting out the results from 73·6 to 66·7 per cent. they form the intermediate curve shown in fig. 1, which on a more open scale is found to indicate a maximum at a strength of 75·0 per cent. of the bromide, and at a temperature of 19°; that is, somewhat beyond the point at which the determinations become impossible owing to the cloudiness and dissociation of the solution. This indicated that the hydrate was probably an octohydrate, which contains 75·261 per cent. To establish this more satifactorily, a quantity of a 73-per-cent. solution was allowed to deposit a few crystals, and these after being drained were analysed and gave the values

Sn, 20·662, Br, 35·011, H_2O (by difference), 24·327,

theory for $SnBr_4\,8H_2O$ requiring

Sn, 20·334, Br, 34·926, H_2O, 24·739.

This octohydrate, as may be inferred from what has been said above, cannot be melted without becoming decomposed and cloudy; but if heated to a higher temperature till clear, and then cooled without stirring, it may generally be cooled to atmospheric temperatures and crystallized without decomposing. By repeatedly crystallizing in this way a sample was prepared for the determinations. The crystals themselves, however, on being kept for any length of time, or on being scratched, generally become cloudy and dissociated.

The heat-capacity and heat of fusion determinations with this substance could not be made in the ordinary manner, as it would have been impossible to see whether, on cooling in the platinum bottle, it had decomposed or not. Fortunately it easily superfuses, and by taking advantage of this property it was found possible to determine its heat of dissolution both in the solid and liquid condition at the same temperature, and from these the heat of fusion may be deduced. The substance in these determinations was enclosed in a glass bulb, which was broken under the surface of the water. The results, as will be seen, are not very concordant. This may be due to the fact that the samples used were different preparations, and may have been of different degrees of purity. The same preparation, however, was used in the first-quoted determination with the solid and in the first with the liquid, and similarly with the two second determinations, and these two pairs are concordant in the values which they give for the heat of fusion, 10,230 cal. according to the first determinations, 10,176 cal. according to the second.

The anhydrous tetrabromide used was not satisfactorily pure. The commercial sample obtained was found, in spite of special care having been taken in its preparation, to contain a considerable amount of dibromide, for, on melting it, globules of the latter separated. After twelve fractionations by crystallizing, a sample was obtained with 8 per cent. of the dibromide, but further fractionation did not appear to reduce the amount of this impurity: indeed the formation of the dibromide seems to occur spontaneously in the tetrabromide, for it was often noticed that a specimen which was perfectly clear and free from any visible globules of the dibromide, would, on being melted again, leave particles of the latter adhering to the glass; yet in no case was the presence of bromine indicated either by colour or smell. When water is added to the tetrabromide, visible traces of bromine are liberated.

The values obtained for the heat of dissolution of the anhydrous salt are not very concordant, but this may be due to the different proportions of water used in the two determinations.

Hemiheptahydrate of Sodium Hydroxide ($NaOH,3\frac{1}{2}H_2O$).—The heat of formation of this hydrate (for a description of which see Trans. Chem. Soc. 1893, p. 893) from the monohydrate and water was determined. This does not constitute an unexceptionable instance; for one of the constituents itself being a hydrate, and not a simple compound, the results are complicated by the fact that the heat of fusion of this constituent may not represent its true heat of fusion, but may include some heat absorption due to partial dissociation on melting.

In dealing with the monohydrate it was found that after it had solidified in the platinum bottle containing the thermometer, it was necessary to heat it very slowly indeed to remelt it, so as to avoid breaking the bulb of the thermometer by unequal expansion. Two thermometers were destroyed by heating too rapidly.

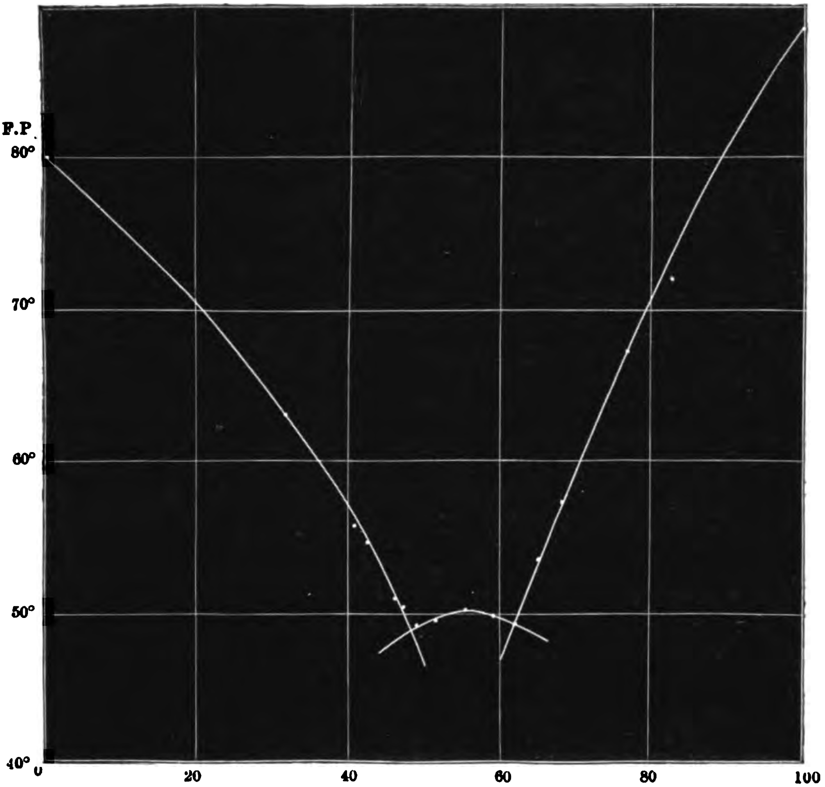
Compound of Benzene and Azobenzene.—The values for benzene will be found in the Proc. Roy. Soc. *loc. cit.* The solvent used in determining the heat of dissolution was benzene.

On calculating the results, the heat of combination, both in the liquid and solid condition, was found to be negative. It appears very improbable, however, that this should be a correct result in a case where we have direct combination occurring in the absence of a solvent, and without the formation of any secondary products: in every case, except one doubtful one, where the heat of formation of a hydrate has been measured, the value is a positive quantity (see Chem. Soc. Trans. 1887, p. 77). The explanation here may be that the measurement of the heat of fusion of benzene and of the compound is at fault: in both cases the heat-capacity in the solid condition is greater than that in the liquid condition, which is exceptional and which is generally taken to imply that the heat absorbed in fusion is absorbed gradually over an appreciable range of temperature, and not all at the ordinary fusing-point, so that the heat of fusion as measured at the fusing-point itself is too low, and the heat-capacity of the solid as measured in its neighbourhood is too high.

Compounds of Naphthalene with Metadinitrobenzene and with Dinitrobenzene.—These compounds, and several others of a similar character, were obtained by Hepp (*Annalen*, ccxv. p. 379) by mixing solutions in benzene of the two constituents and crystallizing. The presence of any solvent appeared, however, to be superfluous, and preparations of them were made by mixing the substances in the proper proportions when liquid. It seemed desirable, however, to obtain more evidence than that heretofore existing as to the substances formed being really definite compounds. Series of freezing-point determinations were, therefore, made, the results of which are given in Table V. and figs. 2 and 3. These prove the definite existence of the compounds in question: we have a figure made up of three curves (fig. 2), the first one representing the lowering of the freezing-point of dinitrobenzene by naphthalene, the last the lowering of the freezing-point of naphthalene by dinitrobenzene; the intermediate one is evidently an independent curve with two branches and represents, therefore, the crystallization of some third substance; the maximum of this curve is situated at 57 per cent. of dinitrobenzene, which agrees well with equimolecular proportions, these requiring 56·7 per cent.

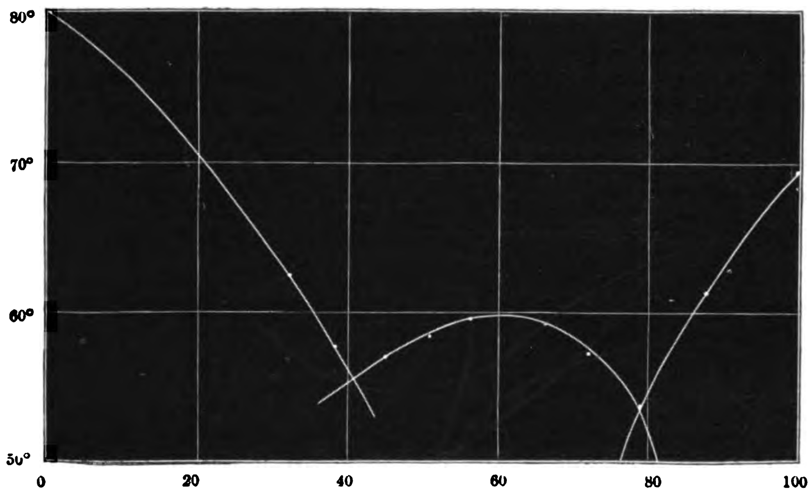
The results in the case of dinitrotoluene are similar, except

Fig. 2.—Freezing-points of Solutions of Metadinitrobenzene and Naphthalene.



Per cent. Dinitrobenzene.

Fig. 3.—Freezing-points of Solutions of Dinitrotoluene and Naphthalene.



Per cent. Dinitrotoluene.

that the range of strength over which the compound crystallizes is considerably greater. Here the maximum of the curve is at about 59·5 per cent., equimolecular proportions requiring 58·7 per cent.

In the heat of dissolution determinations it was necessary to use a solvent—benzene—which was not one of the constituents of the compounds, a slight modification in the ordinary procedure was therefore necessary. Since the heat of formation of the compound AB is given by the difference between the heat of dissolution of AB and of A and B separately, the calorimetric liquid must have the same composition at the end of each of the determinations or the reactions will not be comparable, the heat of dissolution A must be determined in a solvent containing already a corresponding proportion of B; similarly with the heat of dissolution of B. An equivalent proportion of naphthalene was, therefore, added to the benzene before determining the heat of dissolution of nitrobenzene or nitrotoluene in it, and equivalent proportions of either of the latter added before determining that of the naphthalene. In the table will also be found the values for the heat of dissolution of the various constituents in pure benzene, although these are not of any service for the present calculations.

The values for the heat-capacity and heat of fusion of naphthalene have already been given in the Proc. Roy. Soc. *loc. cit.*

Table II. contains also values for the heat of fusion and heat-capacity of aluminium bromide. These were determined because it was thought that the hydrate with $12H_2O$ would prove a suitable instance for investigation, since Roozeboom states that it melts at a few degrees above 100°[*]. It was found, however, that in melting it partially decomposed, forming some less fusible compound, for the liquid was always cloudy, and would not become clear even on boiling. Whatever the substance is which thus separates, it appears to enter into combination again on cooling, for the addition of a little water forms a clear solution, no basic salt or alumina being apparently present. This behaviour was observed both with a preparation made by the author and with one made by Messrs. Kahlbaum.

Results Obtained.

The values for the apparent heat of combination in the two conditions are given in Table VI., arranged in the order of magnitude of the heat of combination per molecule of water, or analogous constituent. The values for the heat of dissolution which give the heat of combination are contained in the first two columns. The latter, of course, apply to the temperatures at which the heat of dissolution was determined, and this varies in different cases from 19° to 15°.

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[*] I have unfortunately mislaid the reference to the paper containing this statement.

We may conclude with a fair degree of confidence that, even in the case of the most stable compound investigated, its constituents are dissociated to a certain extent in the liquid condition, and, therefore, that the heat evolved on mixing the liquids should be less than that evolved on combining the solids, but, it will be seen, that in the first four instances the reverse is the case, the apparent heat of combination of the liquids is the greater of the two quantities, and we must therefore conclude that this apparent heat of combination is not the true heat of combination, and that the hypothesis on which it was taken to be the true heat of combination—namely, that the heat of fusion of the compound is equal to the sum of that of its constituents—is incorrect (see p. 510). In order to account for the apparent heat of combination of the solids (H′) being less than that of the liquids (H), it is necessary, as will be seen from the equations given on pp. 510, 511, that the heat of fusion of the compound should be *less* than the sum of those of its constituents, and this is the direction in which we should naturally expect inequality, if any such exist: for when two substances have expended some of their residual affinity in combining with each other, they will have a smaller supply available with which to combine with themselves, when they form aggregates on passing into the solid condition, and their heat of fusion when combined will, therefore, be less than when uncombined. The only one of the seven substances examined in which the heat of combination in the liquid form is considerably less than that in the solid is the hydrate of pinacone: this does not, of course, necessarily imply that it is an exception as to the heat of fusion of the compound being less than the sum of those of its constituents, but simply that the hydrate may be dissociated to a very large extent on fusion.

The other two exceptional instances are exceptional also as regards the negative value for the heat of their formation. In the case of benzene combining with azobenzene this has already been mentioned, and a probable explanation of it has been offered: a similar fact is noticed in the case of the compound of naphthalene with dinitrobenzene where there are no grounds for suggesting a similar explanation, but the values in this case are so small that the heat of combination might well be a positive quantity within the limits of experimental error, the values given depending, as they do, on so many different measurements.

TABLE I.—Determinations of the Heat-Capacity and Heat of Fusion.

Substance.	F.P.	Weight taken. w.	τ.	Water equiv. of bottle &c. w'.	Water equiv. of calorimeter &c.	t'.	$t-t'$.
1. Azobenzene	66°·8	31·67	97°·22	2·3	608·42	21°·76	3°·2364
2. „	„	„	96·08	„	„	22·08	3·2004
3. „	„	„	74·54	„	„	21·42	2·6143
4. „	„	„	74·14	„	„	21·46	2·6696
5. „	„	35·01	58·95	„	„	19·69	1·3394
6. „	„	„	58·99	„	„	19·46	1·2864
7. Azobenzene and benzene	35·8	23·287	70·65	1·93	„	21·33	2·4656
8. „ „	„	„	69·86	„	„	21·31	2·4814
9. „ „	„	„	42·23	„	„	20·01	1·8579
10. „ „	„	„	42·01	„	„	19·87	1·8221
11. „ „	„	„	30·97	„	„	18·20	0·3317
12. „ „	„	„	31·40	„	„	18·18	0·3465
13. NaOH, H_2O	64·3	55·08	99·24	2·8	1841·90	21·87	3·222
14. „	„	„	96·50	„	„	22·11	3·112
15. „	„	54·922	70·50	„	„	21·75	2·571
16. „	„	56·225	56·92	2·3	608·42	22·39	1·461
17. „	„	„	56·98	„	„	21·01	1·467
18. NaOH, $3\frac{1}{2}H_2O$	15·55	39·70	60·82	„	„	23·15	2·235
19. „	„	„	61·96	„	„	21·91	2·365
20. „	„	39·93	9·93	„	„	23·70	−3·678
21. „	„	„	9·71	„	„	23·87	−3·676
22. „	„	„	−15·00	„	„	23·81	−4·559
23. „	„	„	−13·67	„	„	23·98	−4·428
24. Pinacone hexhydrate	45·42	29·37	78·03	2·32	606·56	18·758	5·959
25. „ „	„	„	77·69	„	„	18·872	5·926
26. „ „	„	„	49·95	„	„	18·612	4·569
27. „ „	„	„	49·40	„	„	18·006	4·549
28. „ „	„	„	39·33	„	„	15·526	0·702
29. „ „	„	„	39·86	„	„	15·378	0·726
30. Pinacone	40·48	28·09	69·19	2·33	„	14·855	1·869*
31. „	„	„	68·00	„	„	15·044	1·842*
32. „	„	27·86	44·43	1·70	„	15·982	1·933†
33. „	„	„	44·43	„	„	15·105	1·881†
34. „	„	27·31	−20·10	2·43	„	14·145	0·863‡
35. „	„	„	−20·28	„	„	14·937	0·862‡

36. Metadinitrobenzene	88·25	44·438	123·80	2·33	606·56	18·024	4·864
37. " "	"	"	121·31	"	"	18·052	4·827
38. " "	"	"	93·24	"	"	17·544	3·844
39. " "	"	"	93·06	"	"	16·989	3·842
40. " "	"	41·92	69·32	2·43	"	16·224	1·451
41. " "	"	"	67·78	"	"	15·760	1·395
42. Metadinitrobenzene and Naphthalene	50·17	37·01	92·75	"	"	16·822	3·606
43. " " "	"	"	92·36	"	"	16·323	3·627
44. " " "	"	36·84	56·99	"	"	15·756	2·554
45. " " "	"	"	56·61	"	"	15·779	2·549
46. " " "	"	"	40·08	"	"	13·991	0·760
47. " " "	"	"	38·94	"	"	13·848	0·716
48. Dinitrotoluene	69·19	41·61	99·85	"	"	17·043	4·124
49. "	"	"	98·91	"	"	17·060	4·121
50. "	"	42·17	73·00	"	"	16·957	3·357
51. "	"	"	72·34	"	"	17·405	3·356
52. "	"	"	49·13	"	"	14·233	0·942
53. "	"	"	48·45	"	"	14·554	0·923
54. Dinitrotoluene and Naphthalene	59·78	35·63	94·14	"	"	16·608	3·605
55. " " "	"	"	93·97	"	"	16·910	3·621
56. " " "	"	39·24	65·35	"	"	16·116	3·106
57. " " "	"	"	64·81	"	"	16·168	3·054
58. " " "	"	"	49·17	"	"	15·430	0·904
59. " " "	"	"	48·58	"	"	15·024	0·897
60. Tin Tetrabromide	29·36	103·62	69·80	"	"	16·370	2·189
61. " "	"	"	68·78	"	"	17·009	2·179
62. " "	"	"	68·29	"	"	15·145	2·171
63. " "	"	"	39·52	"	"	14·980	0·507
64. " "	"	"	38·20	"	"	14·382	0·524
65. " "	"	"	−17·65	"	"	15·637	0·608
66. " "	"	"	−19·56	"	"	15·220	0·645
67. Aluminium Bromide	94·69	84·40	125·21	2·33	"	16·935	3·557
68. " "	"	"	125·16	"	"	16·370	3·557
69. " "	"	"	99·29	"	"	15·902	3·012
70. " "	"	"	99·02	"	"	15·803	3·014
71. " "	"	"	88·90	"	"	15·177	1·672
72. " "	"	"	88·29	"	"	15·530	1·651

* The pinacone remained liquid throughout the determination. † Solidified during the determination. ‡ Solid throughout.

TABLE II.—Heat Capacity and Heat of Fusion Results.

Experiment.	Substance.	Property.	Per 1 gram.	Per gram-molecule.	Molecular weight.	Temperature.
—	Water.	Heat-cap. liq. = C.	1	18	18	0°
—	„	Heat-cap. sol. = *c*.	·5243	9·437	„	0
—	„	Heat of fusion.	79·25	1426·5	„	0
—	„	C—*c*.	·4757	8·563	„	—
—	Benzene.	Heat-cap. liq.	·3957	30·865	78	5·41
—	„	„ sol.	·4600	35·880	„	5·41
—	„	Heat of fusion.	29·433	2295·8	„	5·41
—	„	C—*c*.	—·0643	—5·015	„	—
1 & 3. 2 & 4.	Azobenzene.	Heat-cap. liq.	·4613 ·4055 } ·4334	78·88	182	97—22
5. 6.	„	„ sol.	·3730 ·3674 } ·3702	67·38	„	59—19
3. 4.	„	Heat of fusion.	26·220 27·486 } 26·853	4887·2	„	66·8
—	„	C—*c*.	·0632	11·50	„	—
7 & 9. 8 & 10.	Benzene and Azobenzene.	Heat-cap. liq.	·5077 ·5719 } ·5398	140·35	260	70—21
11. 12.	„	„ sol.	·5959 ·6020 } ·5989	155·71	„	42—20
9. 10.	„	Heat of fusion.	33·774 32·872 } 33·323	8664·0	„	35·8
—	„	C—*c*.	—·0591	—15·36	„	—
—	Sulphuric Acid.	Heat-cap. liq.	·3355	32·879	98	10·35
—	„	„ sol.	·2721	26·666	„	10·35
—	„	Heat of fusion.	24·031	2355·0	„	10·35
—	„	C—*c*.	·0634	6·213	„	—
—	Monohydrate of Sulphuric Acid.	Heat-cap. liq.	·4430	51·388	116	8·52
—	„	„ sol.	·2273	26·367	„	8·52
—	„	Heat of fusion.	39·918	4630·5	„	8·52
—	„	C—*c*.	·2157	25·021	„	—
13 & 15. 14 & 15.	Monohydrate of Soda.	Heat-cap. liq.	·6458 ·7011 } ·6735	39·061	58	98—22
16. 17.	„	„ sol.	·4170 ·4006 } ·4088	23·709	„	57—22
15.	„	Heat of fusion.	62·151	3613·1	„	64·3
—	„	C—*c*.	·2647	15·352	„	—

18. 19.	3·5 hydrate of Soda.	Heat-cap. liq.	·8506 ·8463	·8484	87·387	103	61—22
22 & 20. 23 & 21.	,,	,, sol.	·4772 ·4285	·4528	46·638	,,	−15—10
20. 21.	,,	Heat of fusion.	45·788 45·467	45·628	4699·7	,,	15·55
—	,,	C—*c*.		·3956	40·749	,,	—
30. 31.	Pinacone.	Heat-cap. liq.	·6425 ·6647	·6536	77·13	118	69—15
34. 35.	,,	,, sol.	·4705 ·7544	·4624	54·56	,,	−20—14
32. 33.	,,	Heat of fusion.	26·443* 24·017†	25·230	2977·1	,,	40·48
—	……	C—*c*.		·1912	22·57	—	—
24 & 26. 25 & 27.	Pinacone hydrate.	Heat-cap. liq.	·9461 ·9451	·9456	213·71	226	78—19
28. 29.	,,	,, sol.	·5297 ·5332	·5315	120·12	,,	39·15
26. 27.	,,	Heat of fusion.	73·354 73·143	73·249	16554·3	,,	45·42
—	,,	C—*c*.		·4141	93·59	,,	—
36 & 38. 37 & 39.	Metradinitro-benzene.	Heat-cap. liq.	·4021 ·4390	·4206	70·53	167·7	123—18
40. 41.	,,	,, sol.	·3396 ·3323	·3359	56·32	,,	68—16
39. 40.	,,	Heat of fusion.	22·835 22·491	22·663	3800·1	,,	88·25
—	,,	C—*c*.		·0847	14·21	,,	—
42 & 44. 43 & 45.	Metradinitro-benzene and naphthalene.	Heat-cap. liq.	·4257 ·4307	·4282	126·48	295·4	93—17
46. 47.	,,	,, sol.	·4136 ·4036	·4086	120·69	,,	39—14
44. 45.	,,	Heat of fusion.	22·347 22·465	22·406	6618·3	,,	50·17
—	,,	C—*c*.		·0196	5·79	,,	
	Naphthalene.	Heat-cap. liq.		·4824	61·60	127·7	102—80
	,,	,, sol.		·3612	46·13	,,	73—18
	,,	Heat of fusion.		35·625	4549·3	,,	79·86
	,,	C—*c*.		·1212	15·55	,,	

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* At the temperature at which solidification occurred in the experiment (15°·982) it was 21·760.

† ,, ,, ,, ,, ,, ,, ,, (15° 105) ,, 19·165 (see p. 513).

Table II. (*continued*).

Experiment.	Substance.	Property.	Per 1 gram.	Per gram-molecule.	Molecular weight.	Temperature.
48 & 50. 49 & 51.	Dinitrotoluene.	Heat-cap. liq.	·3818 ·3791 } ·3804	69·10	181·7	99—17
52. 53.	„	„ sol.	·3308 ·3340 } ·3324	60·38	„	49—14
50. 51.	„	Heat of fusion.	26·697 26·247 } 26·472	4808·7	„	69—19
—	„	C—*c*.	·0480	8·72	„	
54 & 56. 55 & 57.	Dinitrotoluene and Naphthalene.	Heat-cap. liq.	·3928 ·4270 } ·4099	126·80	309·4	94—17
58. 59.	„	„ sol.	·3524 ·3514 } ·3519	108·86	„	49—15
56. 57.	„	Heat of fusion.	27·265 26·788 } 27·027	8360·8	„	59·78
—	„	C—*c*.	·0580	17·94	„	—
67 & 69. 68 & 70.	Aluminium Bromide.	Heat-cap. liq.	·1260 ·1302 } ·1281	34·106	266·3	125—17
71. 72.	……	„ sol.	·1354 ·1355 } ·1354	36·070	„	89—15
69. 70.	……	Heat of fusion.	8·102 8·017 } ·8090	2154·4	„	94·69
—	……	C—*c*.	—·0074	—1·964	„	—
62 & 63. 60 & 64. 61 & 63. 61 & 64.	Tin Tetrabromide.	Heat-cap. liq.	·0821 ·0964 ·0845* ·1040* } ·0909	39·668	436·4	— 69—16
65. 66.	……	„ sol.	·0837 ·0852 } ·0845	36·875	……	—19—15
63. 64.	……	Heat of fusion.	7·000 6·616 } 6·808	2970·9	……	29·36
—	……	C—*c*.	·0064	2·793	—	
From heat of dissolution.	Tin Tetrabromide octohydrate.	Heat of fusion at 14·85°.	17·588	10203	580·1	14·85

* Half weight allowed to these determinations.

TABLE III.—Heat of Dissolution Results.

Substance.	Weight taken. *w.*	Solvent.	Water equiv. of solvent and apparatus. W.	*t.*	*t′−t.*	Molec. Heat of Dissolution. M.
H_2SO_4 liq.	……	$\propto H_2O$	……	17·91	……	21093
,, sol.	……	,,	……	,,	……	18691
H_2SO_4, H_2O liq.	……	,,	……	,,	……	14426
,, ,, sol.	……	,,	……	,,	……	10578
$(C_6H_5)_2N_2$ sol.	8·068	$147C_6H_6$	222·41	19·73	−0·9982	−5008 } −5067
,,	8·270	$133C_6H_6 + (C_6H_5)_2N_2$	226·00	19·51	−1·0304	−5125
,, liq.	……	……	……	(19·62)	……	− 656 − 773
$(C_6H_5)_2N_2$, C_6H_6 sol.	11·386	$150C_6H_6$	225·88	19·90	−1·5230	−7860 } −7915
	11·611	$148C_6H_6 + (C_6H_5)_2N_2$	232·15	19·78	−1·5287	−7969
,, ,, liq.	……	……	……	(19·84)	……	950 841
NaOH, H_2O sol.	10·306	$188H_2O$	613·17	18·72	1·424	4912 } 5103
,,	6·602	$294H_2O$	610·68	18·89	0·987	5294
,, liq.	……	……	……	(18·80)	……	8017
NaOH, $3\frac{1}{2}H_2O$ liq.	17·711	$299H_2O$	621·25	18·77	0·596	2152 } 2185
,,	17·639	$300H_2O$	621·16	18·66	0·611	2217
,, sol.	……	……	……	(18·76)	……	2646
$C_6H_{14}O_2$, $6H_2O$ sol.	4·040	$1830H_2O$	610·06	14·75	−0·295	−10071 } −10077
,,	4·144	,,	610·15	14·79	−0·303	−10083
,, liq.	……	……	……	(14·77)	……	+ 4071
$C_6H_{14}O_2$ sol.	1·926	$2040H_2O$	607·34	14·79	0·080	2982 } 3036
,,	2·089	$1880H_2O$	607·49	14·99	0·090	3090
,, liq.	……	……	……	(14·89)	……	+ 5436

Table III. (*continued*).

Substance.	Weight taken. w.	Solvent.	Water equiv. of solvent and apparatus. W.	t.	t′−t.	Molec. Heat of Dissolution. M.
$SnBr_4$ sol.	9·707	$1500H_2O$	607·01	14·86	0·559	15251 } 15543
"	18·890	$770H_2O$	607·85	14·87	1·128	15835
" liq.	......	$1140H_2O$	......	(14·87)	......	184 73
$SnBr_4,8H_2O$ sol.	14·382	$1340H_2O$	611·40	14·86	−0·285	− 6249 } −6636
"	16·561	$1170H_2O$	611·93	14·92	−0·292	− 7023
" liq.	14·805	$1300H_2O$	611·10	14·80	·166	3981 } 3567
"	14·940	$1190H_2O$	611·18	14·84	·133	3153
Naphthalene sol.	4·265	$204C_6H_6$	228·35	14·89	− ·622	−4249 } −4268
"	4·307	$202C_6H_6$	228·36	14·80	− ·633	−4286
" liq.	......	$203C_6H_6$	......	14·85	......	− 730
$C_6H_4(NO_2)_2$ sol.	5·650	$202C_6H_6+C_{10}H_8$	230·72	14·13	− ·556	−3811
" liq.	......	"	......	14·13	......	−1064
$C_7H_6(NO_2)_2$ sol.	6·093	$203C_6H_6+C_{10}H_8$	230·67	14·11	− ·720	−4949
" liq.	......	"	......	14·11	......	− 621
$C_6H_4(NO_2)_2$ sol.	5·537	$206C_6H_6$	228·61	14·81	− ·474	−3279
" liq.	......	"	......	"	......	− 523
$C_{10}H_8$ sol.	4·270	$204C_6H_6+$ $C_6H_4(NO_2)_2$	230·67	14·53	− ·635	−4389
" liq.	......	"	......	"	......	− 856
$C_7H_6(NO_2)_2$ sol.	6·146	$201C_6H_6$	228·62	14·93	− ·718	−4855
" liq.	......	"	......	"	......	− 919
$C_{10}H_8$ sol.	4·382	$198C_6H_6+$ $C_7H_6(NO_2)_2$	230·73	14·10	− ·620	−4168
" "	......	"	......	"	......	− 642
$C_6H_4(NO_2)_2+C_{10}H_8$ sol.	9·607	$209C_6H_6$	230·41	14·81	−1·156	−8188
" " liq.	......	"	......	"	......	−1775
$C_7H_6(NO_2)_2+C_{10}H_8$ sol.	10·423	$202C_6H_6$	230·57	14·15	−1·377	−9404
" " liq.	......	"	"	"	......	−1862

TABLE IV.—Freezing-points of Solutions of Tin Tetrabromide.

Per cent. $SnBr_4$.	Freezing-point.
Tin Tetrabromide Crystallizes.	
100	29°·36.
97·58 to 76	Cloudy on cooling. No crystallization at −70°
73·43	Clear on cooling. No crystallization at −70°
The Octohydrate Crystallizes.	
73·63	Cloudy. F.-p. at 18·9?
72·72	18·41
72·53	18·51
72·26	18·20
71·97	18·41
71·26	17·58
71·24	17·17
70·97	16·85
68·47	14·99
67·82	12·51
67·12	10·13
66·70	9·62
62·18	None at −50°
Water Crystallizes.	
56·36	−33°·5
49·74	−20·0
42·47	−16·0
26·97	− 7·5

TABLE V.—Freezing-points of Solutions of Metadinitrobenzene and of Dinitrotoluene in Naphthalene.

Per cent. Dinitrobenzene.	Freezing-point.	Per cent. Dinitrotoluene.	Freezing-point.
100	88°·25	100	69°·19
82·24	71·7	87·40	61·02
75·99	67·2	79·15	53·58
67·52	57·5	71·50	57·72
66·47	54·6	66·20	59·27
64·58	53·63	56·40	59·58
61·54	49·4	50·91	58·75
59·34	50·06	44·82	57·20
56·05	50·17	38·36	57·72
52·65	49·91	32·87	62·37
49·03	49·24	0	79·86
47·21	50·5		
45·88	50·89		
42·66	53·63		
41·01	55·6		
32·42	62·9		
0	79·86		

TABLE VI.—Heat of Combination of the Compounds in the Liquid and Solid Condition.

Compound.	Heat of Combination.		Differences.	Heat of Combin. per 1 mol. H_2O &c.	$D_a + D_b - D_{ab}$*.	
	As Liquids.	As Solids.			As Liquids.	As Solids.
H_2SO_4, H_2O	6667	6533	134	6667	0+21093−14426	−1580+18691−10578
$NaOHH_2O, 2{\cdot}5H_2O$ ..	5832	3783	2049	2333	0+ 8017−2185	−3966+5103+2646
$SnBr_4, 8H_2O$	14906	9748	5158	1863	0+18473−3567	−12431+15543+6636
$C_7H_6(NO_2)_2, C_{10}H_8$ ..	599	287	312	599	−621−642+1862	−4949−4168+9404
$C_6H_{14}O_2, 6H_2O$	1365	3792	−2427	228	0+5436−4071	−9321+3036+10077
$(C_6H_4)(NO_2)_2, C_{10}H_8$ ..	− 145	− 12	− 133	− 145	−1064−856+1775	−3811−4389+8188
$(C_6H_5)_2N_2, C_6H_6$	−1610	−369	−1241	−1610	0−715−895	−3217−5067+7915

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* D^a represents the heat of dissolution of the water, naphthalene, or benzene, D^b heat of the other constituents, and D_{ab} that of the compound.

LI. *On* Helmholtz's *Electrochemical Theory, and some Conclusions deduced from the same. By* F. RICHARZ.

To the Editors of the Philosophical Magazine.

GENTLEMEN,

PROFESSOR G. JOHNSTONE STONEY, in his paper on the "Electron," or Atom of Electricity, in the Philosophical Magazine of October 1894, very rightly draws attention to the fact that he expressed himself first, with regard to Faraday's law, at the Belfast Meeting of the British Association in August 1874, as follows:—"For each chemical bond which is ruptured within an electrolyte a certain quantity of electricity traverses the electrolyte, which is the same in all cases."

Professor G. J. Stoney calls this smallest quantity of electricity the "Electron," and estimates it at 3×10^{-11} of the C.G.S. electrostatic unit of electricity.

In this view, therefore, he anticipated Helmholtz in his Faraday Lecture in April 1881. Helmholtz, however, then propounded further the hypothesis that, "in the case also of non-electrolytes, the 'Valencies' are charged with the same atoms of electricity." Helmholtz explains, moreover, the grounds for the supposition that the attraction between the electrons is the most essential and the greatest part of chemical force. The old electrochemical theory of Berzelius acquired herewith an entirely new form through Helmholtz in respect of the quantity of the atom charges, and deserves therefore the title of "Helmholtz's Electro-chemical Theory."

Without knowing Prof. G. Johnstone Stoney's calculation of the "Electron," I also, in a paper "Ueber die electrischen Kräfte der Atome," read before the Niederrheinische Gesellschaft für Naturkunde on the 1st Dec. 1890 and 12th Jan. 1891*, calculated the electron, and first attached thereto calculations fitted to decide whether "the forces operating in the atoms of a molecule have the same order of magnitude as the electrostatic attraction of the valency-charges."

That this is the case I had then already proved, in respect to the dissociation heat N_2O_4 into $2NO_2$, and I_2 into 2I.

I have further assumed that both atoms of a molecule revolve round each other with a constant velocity, which is given by Boltzmann's kinetic theory of polyatomic gases.

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* F. Richarz, *Sitzungsberichte*, Bonn, vol. xlvii. p. 113 (1890); vol. xlviii. p. 18 (1891).

The equation that the centrifugal force is equal to the force of attraction gives for the latter a value nearly equal to that of the attraction of two "electrons" on each other. Further, I put forward at the same time the hypothesis that radiation is caused by the oscillations of the valency-charges. This supposition was not new, as I have since found. His own quotation in his book, 'Theorie der electrischen und optischen Erscheinungen in bewegten Körpern,' Leiden, 1895, page 5, called my attention to the fact that Prof. H. A. Lorentz as early as 1878 attributed light-waves to electrical particles, which are joined to the atoms and which are also assumed in electrolysis [*Verh. d. kgl. Akad. v. Wetenschappen*, 18 Deel, Amsterdam, 1879; notice especially the conclusion, page 112]. Professor Hertz, as he told me, was of a similar opinion; however, he was not attached to the electrochemical theory of Helmholtz, but to the opinion of Victor Meyer and Riecke (*Berliner Chem. Ber.* xxi. p. 946, 1888). But Lorentz's electromagnetic theory of refraction is, like Helmholtz's theory of Dispersion (1892), independent of the size of the valency-charges. From this quantity, the "electron," I have, in my paper mentioned above of the 12th Jan. 1891, calculated that the period of rotation of the two atoms of a molecule round one another is about 10^{-14} seconds. This is the period of the electrodynamic radiation which the electrons of the two atoms give out while they rotate together with the ponderable atoms round one another. It would correspond with ultra-red waves. As the computed value of the period of rotation is only the average value of the different periods of rotation possessed at the same time by different molecules, the emission must give a more or less extended spectrum of dark heat-rays, which spectrum would have its maximum in the region of the average value. Indeed emission of gases is similar, in so far as the latter is only based on increase of temperature. When the period of rotation is accelerated the spectrum might possibly pass into the visible region.

Prof. G. J. Stoney took up the matter of the electrodynamic radiation of oscillating electrons at about the same time as I did, but in other respects (Trans. Roy. Dublin Soc. vol. iv. 1891, p. 585); later also Prof. H. Ebert (*Arch. de Genève*, [3] xxv. p. 489, May 1891).

I next developed the purely kinetic part of my conclusions (Wied. *Ann.* xlviii. March 1893, pp. 467–492). There I have also taken into consideration the dissociation-heat of hydrogen given by Prof. Eilhard Wiedemann. The same I have also made use of for comparison, besides the dissociation-heat of nitric tetroxide and iodine, already made use of in the first publication of 12th Jan. 1891, in the detailed accounts of my electrical calculations (*Münchener Akademie*, Bd. xxiv. p. 1, 13 Jan. 1894, and Wied. *Ann.* Bd. lii. p. 385, 1894).

There I have also added the following calculation. Assuming that molecular magnetism is produced by the rotation of the valency-charges, we obtain for the specific magnetism at saturation-point values which correspond in the order of magnitude with those found by experiment.

Helmholtz's electrochemical theory has meanwhile also been confirmed in other respects by the very interesting calculations of Prof. A. P. Chattock (Phil. Mag. [5] xxxii. p. 285, 1891; xxxiv. p. 461, 1892; xxxv. p. 76, 1893).

I am, Gentlemen,
Yours faithfully,
University of Bonn, April 1895. F. RICHARZ.

LII. *Note on a Simple Graphic Illustration of the Determinantal Relation of Dynamics.* By G. H. BRYAN[*].

IN the whole range of theoretical dynamics there is probably no theorem which is so difficult to fully grasp as the determinantal relation connecting the multiple differential of the initial coordinates and momenta of a system with that of its final coordinates and momenta. This relation, which may almost be regarded as the keystone to the Kinetic Theory of Gases, is conveniently written in the Jacobian form

$$\frac{d(p_1', p_2', \ldots, q_1', q_2', \ldots)}{d(p_1, p_2, \ldots, q_1, q_2, \ldots)} = 1,$$

where $p_1, p_2, \ldots$ are the generalized momenta corresponding to the generalized coordinates $q_1, q_2, \ldots$, and unaccented and accented letters refer respectively to initial values and final values after a fixed interval of time t.

To my mind the difficulty of grasping this result arises from the want of simple graphical illustrations and verifications from first principles not involving the use of the Calculus. The following illustrative examples of its applications to systems with one degree of freedom have afforded me great assistance in understanding the theorem, and I trust that they may prove useful to others.

Consider a particle moving in the straight line OX (fig. 1) under any law of force. Let M be the position of the particle at any instant, and let the velocity of the particle at this instant be represented by the ordinate MP drawn at right angles to OX. Then, since the momentum is proportional to the velocity, the coordinates OM, MP represent the coordinate and momentum of the particle at the given instant, and we may call P the representative point.

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[*] Communicated by the Physical Society: read April 26, 1895.

Now let four such particles of equal mass be projected simultaneously, having the initial coordinates x and $x+\delta x$ and the initial velocities v and $v+\delta v$. The representative points will form a small rectangle P Q R S of area $\delta x \,.\, \delta v$.

Let P′ Q′ R′ S′ be the corresponding representative points at any subsequent instant t.

Then the determinantal relation asserts that the area of the small parallelogram P′ Q′ R′ S′ is equal to that of the rectangle P Q R S.

[Instead of taking four particles we might suppose the points P, Q, R, S to refer to the *same* particle projected with different initial conditions and allowed to move for a fixed time-interval t.]

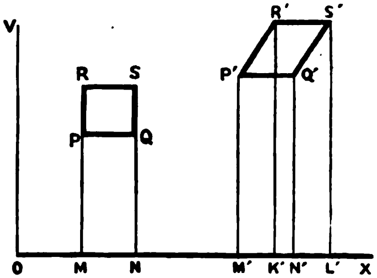
This property may be verified from first principles in the following simple cases:—

Case I. *Let the motion be uniformly accelerated.* Then from the equations

$$v' = v + ft, \qquad x' = x + vt + \tfrac{1}{2}ft^2,$$

and the corresponding equations obtained by substituting $x+\delta x$ for x and $v+\delta v$ for v, it is easy to see (fig. 1) that the

Fig. 1.



parallelogram P′Q′R′S′ has its base P′Q′ parallel to OX and equal to PQ or δx, and its altitude equal to PQ or δv. Therefore

$$\text{area } P'Q'R'S' = \text{area } PQRS.$$

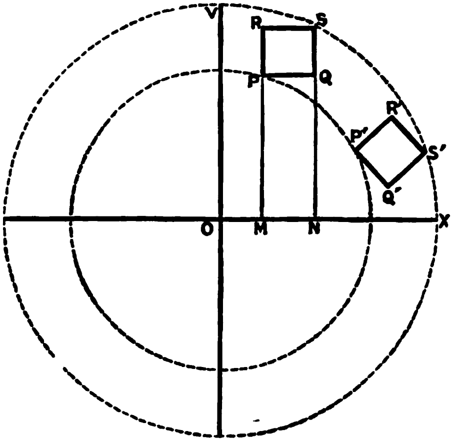
The parallelogram will, however, have undergone a shear, the points R, S having advanced beyond P, Q by an amount $(M'K'=)\delta v\,.\,t$. Hence

$$\cot RPQ = t\,\frac{\delta v}{\delta x},$$

and is proportional to t. As the time increases, the diagonal P′S′ becomes more and more elongated, but the area of the parallelogram remains the same.

CASE II. *Let the motion be simple harmonic*, the acceleration varying as the distance from a fixed point O (fig. 2). Then, by properly choosing the scale of representation of velocity, the representative points of different particles will all describe concentric circles about O with uniform angular velocity. Hence the figure PQRS will be brought into the position P′Q′R′S′ by rotating about O through a certain angle, and the areas of the two figures will of course be equal.

Fig. 2.



Case I. might be deduced as the limit of Case II. by (i.) reducing the scale of representation of velocity so that the circles become projected into ellipses ; (ii.) supposing the centre O to go off to infinity, so that these ellipses gradually become elongated into parabolas.

The case of a repulsive force varying directly as the distance would be a little more complicated ; and it therefore seems hardly worth while to give a proof for it, though the legitimacy of the corresponding inference for this case might be inferred by means of "imaginary projection." The theorem might possibly then be extended to the case of any variable law of force by dividing up the times, and therefore the corresponding spaces decribed, into elements so small that the force might be supposed to vary uniformly with the distance along OX in any single element. This is not put forward as a satisfactory proof, but then the object of this note was to show, not how to prove the theorem, but how to convince oneself of its truth after proving it by highly analytical methods. This I found hard in the case of systems like that of Case I., where a slight variation in the initial conditions (viz. the difference of velocity δv of the points M′K′) causes two such systems to separate indefinitely. I could not see how this was compatible with the multiple differential $(\delta x \, . \, \delta v)$ remaining constant till I had worked out the above explanation. It is a pity that systems with more than one degree of freedom could not be treated by this graphic method, but a similar objection applies equally to the graphic proof of the formula for uniformly accelerated motion of our text-books and to many other valuable illustrations of the principles of dynamics.

LIII. *Note on a Neglected Experiment of* Ampère.

By Silvanus P. Thompson[*].

In the year 1822 Ampère, being at Geneva, showed to De la Rive in his laboratory a number of his now classical experiments on the actions of conductors carrying currents upon other conductors and upon magnets. These are recounted by A. De la Rive in the *Annales de Chimie et de Physique*, xxi. p. 24 (1822).

Amongst these experiments there is one that has almost been forgotten, but which, had it been followed up, would assuredly have led Ampère to anticipate by some years the great discovery of Faraday as to the induction of currents.

The experiment was first described by Ampère in October 1821, in a letter[†] to Van Beck. It had been tried in the preceding July. The following is Ampère's own first description of it:—

"Ce que cette expérience prouve directement, c'est que la proximité d'un courant électrique n'en excite point, par influence, dans un circuit métallique de cuivre, même dans les circonstances les plus favorables à cette influence. Voici

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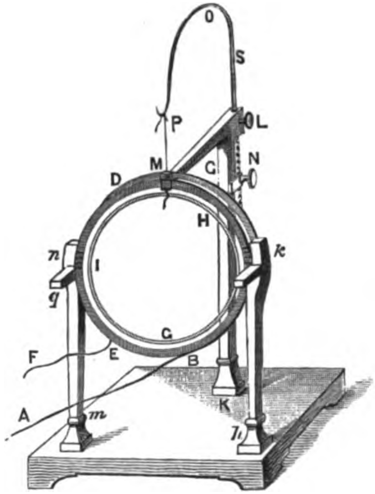
[*] Communicated by the Physical Society: read April 26, 1895.

[†] *Journal de Physique*, t. xciii. p. 447, Oct. 1821. Reprinted at p. 212, vol. ii. of the 'Collection de Mémoires relatifs à la Physique, publiés par la Société française de Physique,' 1885.

l'expérience que je fis alors pour m'en assurer : je formai avec un long fil de cuivre A B C D E F [fig. 1], revêtu d'un

Fig. 1.



ruban, une spirale B C D E dont les tours étaient séparés les uns des autres par la soie de ce ruban ; je disposai cette spirale, comme on le voit dans la fig. 1, sur le pied en bois *h k m n* ; les deux extrémités A et F de ce fil communiquaient avec celles de la pile de douze triades d'un pied carré, dont je me suis servi pour la plupart de mes expériences. La partie supérieure de cette spirale était traversée par un petit tube de verre M, passant entre les spires qui se trouvaient les unes en avant et les autres en arrière de ce tube ; un fil métallique très-fin le traversait sans en toucher les parois intérieures; il était attaché par un bout à la potence K S O P, qu'on faisait monter ou descendre à volonté en tournant le bouton N, et qu'on arrêtait à la hauteur convenable en serrant la vis de pression L ; le cercle mobile G H I était suspendu au bout de ce fil, de manière à être concentrique à la spirale, situé dans le même plan, et très près des spires dont elle se composait. Le pied *h k m n* portait en outre deux petites règles *kp*, *nq*, sur lesquelles on pouvait appuyer les aimants qui devaient agir sur le cercle mobile. Cette disposition m'a paru la plus convenable pour exciter dans ce cercle des courants électriques par influence, si cela était possible ; mais en le présentant à l'action d'un fort aimant, je n'ai pas aperçu qu'il prit aucun mouvement, malgré la grande mobilité de ce genre de suspension."

The experiment of July 1821, being thus unsuccessful, was repeated in 1822 at Geneva, using a more powerful horseshoe magnet lent by Pictet. It is described by De La Rive* in the following terms :—

"La seconde expérience consiste dans l'influence qu'éprouve une lame de cuivre pliée en cercle de la part d'une ceinture de forts courans électriques au milieu desquels elle est suspendue, et qui l'entourent sans la toucher. Cette influence, que M. Ampère avait d'abord crue nulle, a été, à Genève, constatée par lui-même d'une manière très-précise. En présentant à un côté de cette lame un aimant en fer à cheval, très-fort, on l'a vue tantôt s'avancer entre les deux branches de l'aimant, tantôt au contraire en être repoussé, suivant le sens du courant dans les conducteurs environnans. Cette expérience importante montre donc que les corps qui ne sont pas susceptibles, au moyen de l'influence des courans électriques d'acquérir une aimentation permanente, comme le sont le fer et l'acier, peuvent du moins acquérir une sorte d'aimentation passagère pendant qu'ils sont sous cette influence †."

This note, which is textually repeated at p. 285 of Ampère's 'Recueil d'Observations,' is entirely vague on the crucial point whether the attractions and repulsions observed occurred only at times when the current was varying. By reprinting it textually (even the footnote about the instrument, which, however, he changed into the first person and signed with his initial "A"), Ampère accepted De la Rive's version and explanation of the Geneva experiment. Nevertheless a second version was given by Ampère himself ‡ twelve days later on his return to Paris. This document lay unpublished in the Ampère manuscripts belonging to the Académie des Sciences until 1885. It reads as follows :—

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* Read to the 'Société de Physique et d'Histoire naturelle de Genève on Sept. 4, 1822; published first in the *Bibliothèque Universelle*, t. xxi. p. 29 (1822), then in the *Annales de Chimie et de Physique*, t. xxi. p. 47 (1822); reprinted by Ampère at p. 262 of his 'Recueil d'Observations électrodynamiques,' 1822, and again in the 'Collection de Mémoires,' t. ii. p. 328 (1885).

† "L'instrument dont M. Ampère s'est servi pour cette expérience est le même qu'il avait employé lorsqu'il l'essaya au mois de juillet 1820; il a été décrit et figuré dans le *Journal de Physique*." [This is a reference to *Journal de Physique*, xciii. p. 447, Dec. 1821, with a plate showing the apparatus. The same apparatus is depicted in fig. 17, plate vi., of Ampère's 'Recueil d'Observations électrodynamiques' (1822); and is described on p. 170 of that work. There is a discrepancy about the dates; July 1820 is here given, whereas Ampère's first date was given as July 1821.—S. P. T.]

‡ Memoir presented to the Académie des Sciences, September 16, 1822; published for the first time in the 'Collection des Mémoires' by the 'Société française de Physique' (1885), t. ii. p. 329.

"La troisième expérience avait pour objet de savoir si l'on peut produire un courant électrique par l'influence d'un autre courant. Il y a plus d'un an que je l'avais tentée, sans succès, avec l'appareil representé [fig. 1]; mais j'ai réussi avec un appareil absolument semblable, en employant l'excellent aimant en fer à cheval du musée de Genève, que m'avait procuré M. le professeur Pictet. Voici la description de cette expérience." [Here follows the description of the apparatus, word for word almost the same as that above in the description of the unsuccessful experiment of July 1821.] "Le circuit fermé placé sous l'influence du courant électrique dédoublé, mais sans aucune communication avec lui, a été attiré et repoussé alternativement par l'aimant, et cette expérience ne laisserait, par consequent, aucun doute sur la production des courants électriques par influence, si l'on ne pouvait soupçonner la présence d'un peu de fer dans le cuivre dont a été formé le circuit mobile. Il n'y avait cependant aucune action entre ce circuit et l'aimant avant que le courant électrique parcourût la spirale dont il était entouré; c'est pourquoi je regarde cette expérience comme suffisante pour prouver cette production; je me propose, néanmoins, pour prévenir toute objection, de la répéter incessament, avec un circuit formé d'un métal nonmagnétique très pur. Ce fait de la production de courants électriques par influence, très intéressant par lui-même, est d'ailleurs indépendant de la théorie générale de l'action électrodynamique."

There is a discrepancy between the first and second versions, in that while De la Rive says that the attractions and repulsions were in correspondence with the sense of the current in the coil (which we know could not be the case), Ampère says nothing about reversal of the current. As he attributed the effect to the possible presence of iron, it is clear he was expecting an effect due to the continued pressure of the current, not an instantaneous effect at make or break. We know now that this must have been so, and that an unvarying current could have produced no such effects as those described. That this should have escaped the notice not only of Ampère, but also of so skilled an experimenter as De la Rive, is remarkable. But the explanation of the phenomenon, as being due to a temporary magnetization acquired by the nonmagnetic metal, given by De la Rive, and accepted by Ampère, is still more strange. Had no suggestion ever been made that there might possibly be an induction of currents by the action of a magnet, an explanation which ascribed the effects to a sort of temporary magnetism might have been more reasonable. But Ampère had himself already been looking for a possible inductive effect; nor was he alone in the idea that such might exist. Fresnel had on November 6th, 1820, announced to the Academy of Sciences that he had decomposed water by means of a magnet which was laid motionless within a spiral of wire. Emboldened by this announcement, Ampère remarked that he too had noticed something in the way of production of currents from a magnet. But before the end of the year these statements were withdrawn by their authors. Fresnel wrote* to the *Annales de Chimie* explaining the matter. He had surrounded a bar-magnet of steel with a spiral of iron wire, the ends of which dipped into water; and what he had announced on November 6th was that he had found one end of the iron wire to be discoloured and oxidized, while the other became covered with minute bubbles. He now finds that the announcement was premature, that the effects were not sustained by repeating the experiment, and, further, he says he does not believe in the success of Ritter's much earlier attempts to decompose water by a magnet. On behalf of M. Ampère, he added that the latter had indeed found little movements of a magnetic needle by bringing near it a circuit of copper wire (*laiton*) of which a portion was coiled in a spiral around a magnet, but that these movements were not repeated in any constant manner. Further, that these movements were, moreover, so feeble that Ampère would not have published the experiments if the success of Fresnel's, which he thought certain, had not persuaded him that these small agitations were occasioned also by an electric current resulting from the action of the magnet on the spiral in which it was enveloped.

This having occurred in 1820, it is clear that when making the Geneva experiment in 1822 Ampère must have had before him the possibility of induced currents, and chose rather the explanation of a temporary magnetism conferred on the copper loop.

Others in the meantime had tried to repeat Fresnel's observation, and found it erroneous.

Gilbert†, after giving an abstract of Fresnel's reputed discovery, says that he repeated the experiment without finding any discoloration of the iron wire, and concluded that the announcement was premature. Similar conclusions were arrived at by Pohl*.

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* *Ann. Chim. Phys.* xv. 1820, pp. 219–222, "Note sur des Essais ayant pour but de décomposer l'eau avec un aimant."

† Gilb. *Ann.* xlvi. p. 410.

A year or two later, when Arago's rotations were attracting the attention of experimenters, Becquerel † investigated the supposed magnetism of bodies by taking small pieces of them, which he hung within a multiplier-coil of wire in place of the usual magnetic needle, and then turning on a current observed whether they moved or not. He found signs of magnetic action in needles made of peroxide of iron, copper, wood, and even shellac. After narrating his own experiments, he alluded to the Geneva experiment of Ampère, on p. 272, in the following terms:—

"Il résulterait de cette expérience, vu l'action semblable exercée par les deux poles de l'aimant en fer à cheval sur une même portion du circuit, que l'influence du courant électrique aurait développé dans la lame un autre courant électrique, tel qu'on en observe dans un fil métallique qui communique avec les deux poles d'une pile voltaique; mais M. Ampère s'est assuré depuis qu'il n'en est pas ainsi." What steps Ampère had in the meantime taken to assure himself that induction currents did not exist, Becquerel did not state, however.

In 1831 came Faraday's discoveries of the induction of currents by magnets, of the induction of currents by other currents, and of the cause of Arago's rotations. A group of notes ‡ on these discoveries is to be found in December 1831 in the *Annales de Chimie*. It is curious to note the change of views. Becquerel and Ampère's communication to the Academy of January 23, 1832, appears along with abstracts of Faraday's work, and with an account of the experiments of Nobili and Antinori. There is an epitome of facts observed by Becquerel, and another of things to be looked for, by Ampère. This is followed by the following:—"Expériences sur les Courans électriques produits par l'influence d'un autre Courant," par M. Ampère. This article gives a third version of the Geneva experiments.

"Pendant mon séjour à Genève au mois de septembre 1822, M. Auguste de la Rive voulut bien m'aider dans des expériences que je désirais de faire sur la production d'un courant électrique par l'influence d'un autre courant....

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* Oken's *Isis*, 1822, pt. iv. p. 407. Also see remarks signed "P" at the end of an article by Savary in Pogg. *Ann.* viii. p. 368 (1826).

† *Ann. Chim. Phys*, xxv. p. 269.

‡ *Ann. Chim. Phys.* xlviii. 1831, pp. 405–428; see also Pogg. *Ann.* xxiv. 1832, p. 612, and particularly p. 614.

Nous présentions à ce cercle un fort aimant en fer à cheval, de manière qu'un de ses poles se trouvait au dedans et l'autre au dehors du cercle. Dès que nous faisions communiquer avec la pile les deux extrémités du fil conducteur le cércle était attiré ou repoussé par l'aimant, suivant le pole qui répondait à l'intérieur du cercle : ce qui démontrait l'existence du courant électrique qui y était produit par l'influence du courant du fil conducteur. La découverte que vient de faire M. Faraday des courans électriques produits par l'influence d'un aimant, courans qu'avait obtenu Fresnel en 1820, mais qu'il n'avait pas cru suffisamment constatés par ses expériences, m'a porté naturellement à employer le galvanoscope multiplicateur, dont l'illustre chimiste anglais a fait usage, pour constater de nouveau et étudier dans toutes ses circonstances la production d'un courant électrique par un autre courant."

Ampère seems to have considered that the oxidation at first alleged by Fresnel was caused by induction currents arising from the diurnal variations of the magnetism of the stationary magnet. But it is evident that the electromotive forces due to any such cause would be of an order of magnitude utterly inadequate for the purpose. Further, as such currents must necessarily have been in alternate directions during the rise and fall of temperature, the total chemical action at the end would in no way depend upon the intermediate charges, but only upon the difference between the initial and final temperatures. Hence the total electromotive impulse tending to chemical action must have been infinitesimal compared with that due to simply removing the magnet once from the circuit! The third version differs from the former in describing the position of the magnet, and saying that the magnet (which in the original Ampère experiment was brought up after the current had been turned on) was placed in position *before* the circuit was completed.

From that time forward Ampère's experiment seems to have passed into oblivion. One reference to it, however, appeared in 1872, which gives a fourth version, differing not only from the three former, but accompanied by a picture and description of a very different form of apparatus. This description, from the pen of the usually accurate M. Verdet, is to be found at p. 357 of his well-known *Conférences de Physique*. It runs as follows :—

"209. *Expérience d'Ampère et De la Rive.*—Longtemps avant l'époque où Faraday fit la découverte de l'induction, Ampère et De la Rive[*] avaient fait une expérience relative à ces phénomènes et qu'ils n'avaient pas comprise. Ces physiciens cherchaient s'il y avait une action des courants sur des conducteurs placés à distance, par analogie avec les effets d'influence de l'électricité ordinaire; ils entreprirent une série d'expériences avec l'idée préconçue que le phénomène produit par le passage du courant dans un conducteur voisin serait permanent, c'est à dire persisterait pendant tout le temps que le courant traverserait le conducteur; ayant au contraire observé un phénomène instantané, ils regardèrent ce résultat comme un fait singulier ne méritant pas une étude ultérieure. Voici en qui consistait leur expérience: un fil fin de cuivre enroulé en anneau A [fig. 2] était suspendu à un fil de soie sans torsion OC, devant la base d'un électro-aimant BB′, de manière que les plans des spires de l'electro-aimant fussent parallèles au plan de l'anneau. A l'instant où le courant était lancé dans l'électro-aimant, l'anneau était repoussé; mais cette déviation ne persistait pas, et bientôt le fil revenait rigoureusement à la verticale. Si l'on interrompait le courant, on observait une attraction aussi peu persistante que la répulsion."

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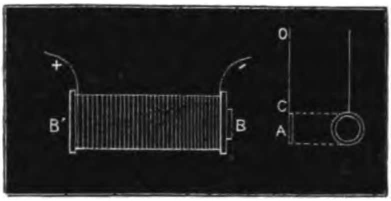
[*] *Bibliothèque Universelle*, septembre 1822, et *Annales de Chimie et de Physique* [2], t. xxi. p. 47 (1822), et t. xxv. p. 272 (1824).

Fig. 2.



The anachronism of representing a soft-iron electromagnet as having been used in 1822 is the strangest part of this description. But the experiment, as described by Verdet, is of interest as being a sort of forerunner of the actions observed in 1884 by Boys*, and in 1887 by Elihu Thomson.

I have repeated the experiment of Ampère in the form originally shown to De la Rive. It is quite easy of performance: but the relatively great moment of inertia of the copper circle masks the purely transitory effect of the impulse which the ring receives each time the current is turned on or off in the outer coil.

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* "A Magneto-electric Phenomenon." Proc. Phys. Soc. vol. vi. p. 218, 1884; Phil. Mag. [5] xviii. p. 216.

LIV. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 142.]

November 21st, 1894.—Dr. Henry Woodward, F.R.S., President, in the Chair.

THE following communications were read:—

1. 'The Pleistocene Beds of the Maltese Islands.' By John H. Cooke, Esq., F.L.S., F.G.S.

For the right understanding of the Pleistocene beds, a previous knowledge of the physiography of the islands and of the earlier sediments is necessary. A full description of the physiography and of the character of the sediments, so far as they are necessary for the understanding of the accumulations forming the subject of the paper, occupies its earlier portion. Especially noticeable is the absence of ordinary anticlinal and synclinal folding, and the predominance of monoclinal faults, which largely affect the character of the surface. These faults were formed prior to the deposition of the Pleistocene beds.

The plateaux of Malta, rising to a height of 600–800 feet above sea-level, occur south of the great east-and-west fault, which has a downthrow to the north. They have no Pleistocene deposits upon their summits.

Three classes of superficial deposits are described:—

I. Valley-deposits, including (*a*) those found on the higher slopes of plains and plateaux, due to subaërial waste and rain-action, containing land-shells and mammalian bones; and (*b*) those situated at the bottoms of valleys, consisting of stratified layers of water-worn sand, gravel, and large pebbles, occurring in such order as to show that the agents which produced them have greatly decreased in intensity.

II. Agglomerates and breccias found along coast-lines and fault-terraces, always at the foot of the fault-terraces, or along the lower slopes of the depressed areas: these accumulations are either submerged or lie at the water-line. Their materials are much water-worn, and land-shells are contained in many of the layers. The agglomerates are in many cases distinctly stratified; and the author concludes that the materials appear to have been swept down, during heavy rainfall, into the waters of land-locked creeks.

III. Ossiferous deposits of caves and fissures, which have been described elsewhere.

2. 'Geological Notes of a Journey in Madagascar.' By the Rev. R. Baron, F.L.S., F.G.S.

The part of the island travelled over may be divided into four sections.

I. *Antananarivo to the East Coast.*—The principal rock is a hornblende granitite-gneiss, but there is also much norite usually containing olivine. The general strike of gneiss and norite along this region is north-west and south-east, or north-north-west and south-south-east. The country is traversed by several large dolerite-dykes.

II. *The Northern Part of the East Coast.*—Dolerite-flows predominate along the coast, and from their character are believed to have flowed from such fissures as are indicated by the dolerite-dykes noted in the preceding section. Some felsites, probably lavas, and felsitic breccias were also observed; also a granitite penetrated by epidiorites, and associated with chiastolite-slates. Many other rocks, schists and eruptives, were found.

III. *The Northern End.*—Sedimentary rocks (sandstones and limestones) are extensively developed in this section, as well as much volcanic material. The sediments are of Jurassic and Cretaceous ages. The volcano Ambohitra is situated on these sediments, and has poured out olivine-basalts. Shells of recent species occur on the mountain-chain at the northern end.

IV. *The North-western Coast and Islands.*—Marine strata of Jurassic, Cretaceous, and Eocene ages are found in this area, together with various igneous rocks including trachyte, foyaite, nepheline-phonolite, hauyne-nepheline-phonolite, andesite, and basalt. South-west of Anorontsanga are four islands—three composed of volcanic rocks, and the fourth, Antanifaly, of nummulitic limestone.

3. 'On a Collection of Fossils from Madagascar obtained by the Rev. R. Baron.' By R. Bullen Newton, Esq., F.G.S.

The fossils forming the subject of this paper were collected in the northern part of the island. The author gives an account of the previous work on the fossils of Madagascar; this is followed by a description of the post-Tertiary, Tertiary, Cretaceous, and Jurassic fossils. The post-Tertiary fossils are for the most part terrestrial shells found on Ambohimarina hill, mainly of species still existing on the island. A few marine forms have been found elsewhere.

A description of species, many of them new, follows; and the author furnishes a list of all recognized fossils from the island, concluding with notes on certain limestones, including a *Globigerina*-limestone and one containing *Girvanella.*

December 5th.—Dr. Henry Woodward, F.R.S., President, in the Chair.

The following communications were read:—

1. 'Supplementary Note on the Narborough district (Leicestershire).' By T. G. Bonney, D.Sc., LL.D., F.R.S., F.G.S., Professor of Geology and Mineralogy in University College, London.

The author revisited this district, briefly described by himself and Mr. Hill in 1878, at Easter 1893 and in September 1894. The old excavations had been greatly enlarged, but little of importance had been disclosed: no dykes and no new junctions with sedimentary rocks. But the crystalline rocks have been recently struck in a fresh locality between Narborough and Huncote, about half a mile west of the pit near the former village. As in that case, the rock lay very near to the surface; here the highest part of the boss was barely covered. The rock is hardly to be distinguished from that of the Narborough pit. The enlargement of the pit south of Enderby has exposed fresh sections of the junction of the slate and syenite, which has been now traced along the whole length of the pit from north to south, and some particulars are added to the former description.

The enlargement of certain of the pits has displayed some interesting sections of Boulder Clay resting upon the crystalline rocks. The latter are not appreciably ice-worn. The fragments in the Boulder Clay, identified by the author, were from the Carboniferous, Trias, Jurassic (especially Lias), and Upper Cretaceous formations. They indicated, in the main, a drift from a more or less north-easterly direction.

2. 'The Tarns of Lakeland.' By J. E. Marr, Esq., M.A., F.R.S., Sec.G.S.

The author has examined several tarns of the English Lake District. In those cases where the stream issues from the tarn over solid rock, he finds either (1) direct evidence that the tarn results from the blocking up of part of a pre-existing valley by drift, causing the deflexion of the water to a direction different from that of the original stream in this locality; or (2) evidence which is perfectly consistent with such an explanation of the origin of the tarn.

Under the circumstances he would submit that tarns cannot be assumed to lie in rock-basins simply because the issuing stream flows over solid rock (and this assumption has been made), but that those who maintain the existence of such rock-basins must prove the occurrence of solid rock entirely around the tarn.

3. 'Description of a New Instrument for Surveying by the Aid of Photography, with some Observations upon the Applicability of the Instrument to Geological Purposes.' By J. Bridges Lee, Esq., M.A., F.G.S.

The instrument described in this paper consists essentially of a photographic camera fitted inside with a magnetic needle, which carries a vertical transparent scale divided and numbered to 360°, and also with cross fibres which intersect at right angles. The fittings and adjustments of the instrument are of such a character that the camera can be accurately levelled and directed towards any point in a horizontal direction, and when a photograph is taken in an ordinary way the bearing of the median vertical plane which bisects the instrument through the photographic lens will be recorded automatically on the face of the photograph.

The vertical fibre (and its image on the photograph) serves as an index to read the bearing; and the same fibre marks by its shadow a line right across the photograph, which marks the median vertical plane on the image. The horizontal fibre is adjusted to mark on the image the horizontal plane which bisects the photographic lens.

The camera rests on a divided horizontal circle, which can be adjusted to a truly horizontal position by levelling-screws. There is a tripod stand and head, with suitable appliances for supporting and adjusting the instrument in position. The camera is provided with a rectilinear doublet lens and iris diaphragm and rack-and-pinion focussing adjustment. It is made of aluminium, and it is surmounted by a telescope adjustable in altitude and fitted with vertical and horizontal webs; and it is also surmounted by a revolvable tubular level.

The details of construction and the peculiar features and adjustments of the instrument are fully described in the paper, and some of the chief purposes to which it may be applied in furtherance of geological research are pointed out. The maker of the instrument is J. J. Hicks, of 8 Hatton Garden.

4. 'The Marble Beds of Natal.' By David Draper, Esq., F.G.S.

A 'crystalline limestone of enormous thickness' was mentioned by Mr. C. L. Griesbach, in 1871 (Q. J. G. S. vol. xxvii. p. 56), as occurring along the lower course of the Umzimkulu, in the county of Alfred, in the southern part of Natal. Since the time of his visit there the country has been opened out by settlers, and some attempts have been made to utilize this marble. The chief mass of this rock is met with at about 7 miles inland, in the Indwendwa hill-range, within the fork formed by the junction of the Umzimkulu and the Umzimkulana, over 700 feet above sea-level, and continuous with the tableland westward. This consists of granite, overlain by the massive marble, roughly stratified, which is denuded north and south of the hill into the gorges of the two rivers, and is continued on the opposite flanks until cut off by faults. The north fault divides it from the Table-mountain Sandstone lying on clay-slate; and the south fault divides the granite from the Table-mountain Sandstone and clay-slate. The bedding of the marble dips towards the rivers, on each of their flanks, and strikes E. and W.

In quality the marble varies from coarse to fine-grained, and in colour from pure white to deep red. The coarse-grained variety contains 5 to 13 per cent. of carbonate of magnesia. Calcareous tufa, in some places several feet thick, has been formed from the marble.

From the junction of the two rivers eastward, slate is seen below Table-mountain Sandstone; and on the latter is a long stretch of the Dwyka Conglomerate to the coast, greatly disturbed for the most part, and pierced by two dolerite-dykes, between which a patch of Ecca Shales is preserved.

The author concludes that the marble was deposited on the granite, and probably on the Malmesbury Slates near by, before they were disturbed; that it does not extend far under the neighbouring hills; and that some of its local detritus indicates that the rivers ran at higher levels within relatively recent times.

December 19th.—Dr. Henry Woodward, F.R.S., President, in the Chair.

The following communications were read:—

1. 'The Lower Greensand above the Atherfield Clay of East Surrey.' By Thomas Leighton, Esq., F.G.S.

This paper embodies the results of the author's examination of the Lower Greensand of East Surrey during the three years 1892–94; and it is stated that two papers published by the Geologists' Association (vol. xiii. pp. 4 & 163) are to be taken as introductory to this one. The area discussed in this paper extends from Leith Hill in the west to Tilburstow Hill in the east; and the divisions of the Lower Greensand chiefly referred to are those hitherto known as the Bargate, Sandgate, and Hythe Beds. The author states that the Lower Greensand of East Surrey shows that formation to consist of beds deposited in a marine estuary or narrow sea, not far from land and within the influence of strong currents, extending generally from N.W. to S.E., so that, without palæontological evidence, no correlation of beds here with those exposed at Sandgate and at Hythe is possible. He arrives at this conclusion by following the outcrop of the various chert-beds, which, after Dr. G. J. Hinde (Phil. Trans. Roy. Soc. vol. clxxvi. 1885), are accepted as of sponge origin (deep-water deposits), and further by following the outcrop of the pebble-beds, described by Mr. C. J. A. Meÿer (Geol. Mag. for 1866, p. 15).

In Part 1 of the paper the author discusses the district to the west of the Mole, and endeavours to show that the view set forth in the Weald Memoir of the Geological Survey, to the effect that between Dorking and Leith Hill the lower horizons of the Lower Greensand undergo a change in composition, although possibly verbally correct, is geologically incorrect, since the lithological change is from south to north, from beds laid down in deep water to beds laid down in shallow water. In his communication to the Geologists' Association of last year, the author showed that the pebble-bed at the base of the Folkestone Sands was at Abinger intimately associated with the Bargate Beds; and he now states that he has identified this pebble-bed in the Dorking-Horsham road section, described by Prof. G. S. Boulger and himself in 1892, and at two other places to the east. The drifts of the same neighbourhood are then discussed, and it is found that at the top of and on both sides of the Lower Greensand escarpment, which, as stated by the Geological Survey, is here sandy throughout, there are gravels obviously deposited by a considerable stream consisting chiefly of Lower Greensand chert (entirely of Lower Greensand material) with, amongst the rougher material, lenticular beds of fine pebbles composed chiefly of débris from the Bargate Beds. Fragments of Lower Greensand chert have been obtained from the alluvium or from the beds of the streams now draining the Weald area to the south of Dorking. The soil over the Weald Clay as far south as Holmwood Common has everywhere yielded to the author fragments of the same chert. Hence it is argued that the chert-beds now seen upon Leith Hill to the west formerly existed over the Weald to the south of Dorking, and that the fragments now lying about the surface have been left by denudation, as described by Dr. G. J. Hinde (*op. cit.*). Since, however, as has been stated, the present Lower Greensand escarpment to the north consists of 'sandy beds' only, there must be a lithological change from south to north (deep-water beds to shallow).

Part 2 of the paper is devoted to the district east of the Mole. Where the escarpment rises above the alluvium of the river, the author finds the Bargate Beds with pebbles (at Park Hill, Reigate) separated from the Folkestone Sands only by a thin bed of Fuller's Earth and a layer of sandy chert. The section is now first described; the dip has been observed and proved, and by measurement this pebble-bed is shown to lie at approximately the same horizon above the Atherfield Clay as when it was last seen west of the Mole. From Reigate eastwards to Tilburstow Hill the same beds are seen in the numerous hollow lanes and pit-sections. The pebble-beds are found approximately on a definite horizon; but whilst they become of less importance eastward, the overlying cherts, first seen at Reigate, become of greater importance in that direction. The thin bed of Fuller's Earth, also first seen at Reigate, thickens to the east likewise.

2. 'On the Eastern Limits of the Yorkshire and Derbyshire or Midland Coalfield.' By W. S. Gresley, Esq., F.G.S.

The author attempts to throw light on the question of the easterly extension of the Yorkshire, Derbyshire, and Nottinghamshire coalfield beneath the newer rocks. He notices the general trend of the strata, the sizes of other British coalfields, the question of the origin of mountains, stratigraphical considerations, and the faults of the North of England. His object is rather to suggest what he believes to be novel ways of treating the subject than of reaching conclusions or locating limits.

3. 'On some Phases of the Structure and Peculiarities of the Iron Ores of the Lake Superior Region.' By W. S. Gresley, Esq., F.G.S.

The author has been studying heaps of ore brought from the region lying south-west of Lake Superior since 1890. He describes certain structural features of the ore-fragments, and discusses the evidences of mechanical movements and chemical alteration exhibited by these fragments.

LV. *Intelligence and Miscellaneous Articles.*

ON ELECTROMAGNETIC TRACTIVE FORCE. BY M. WEBER.

The author summarizes the results of his experiments as follows:—

(1) An iron wire of great length in comparison with its diameter, one end of which is in a magnetic field parallel to the lines of force, experiences a pull in the direction of its length which for unit area (the square centimètre) of the cross-section is $p\sharp = \mathrm{IH} = \kappa \mathrm{H}^2$.

(2) If the magnetic lines of force are at right angles to the longitudinal direction of the wire projecting into the field, the tractive force at right angles to the lines of force is smaller in iron than the force $p\sharp$. The ratio $p\sharp/p\perp$ (where $p\sharp$ and $p\perp$ are the tractive forces parallel and at right angles to the lines of force respectively), which with mean strengths (about $H=100$) is greater than 100, rapidly decreases as the field increases and appears to approach unity.—Wiedemann's *Annalen*, No. 1, 1895.

ON THE INFLUENCE OF MAGNETIZATION ON THE CONSTANTS OF ELASTICITY IN IRON. BY A. BOCK.

The result of this research is stated as follows by the author:—By magnetization the constants of elasticity of soft iron, the modulus of torsion, and the modulus of elasticity are certainly not altered by more than ½ per cent. The series of observations indicate that the flexure diminishes, at the same time the torsion seems also to diminish, while the ratio of the lateral contraction to the longitudinal expansion increases. Iron is more incompressible in the magnetic field. Nothing can be alleged with certainty as to magnetized steel bars. These results are in perfect agreement with the well-known investigations of G. Wiedemann, and they may be deduced from the theory propounded by that author on the assumption of rotating molecular magnets.—Wiedemann's *Annalen*, No. 3, 1895.

ON THE MAGNETIZATION OF IRON BY VERY SMALL FORCES. BY WERNER SCHMIDT.

The experimental results of this research are given by the author in the following statements:—

1. Steel follows small magnetizing forces more rapidly than iron.

2. The magnetization function κ of *mild steel* is greater for small forces than that of iron. In the present case κ (steel) is to κ (iron) as 4 is to 3. The stronger magnetization ordinarily observed in iron is only met with in greater magnetizing forces, for instance, $H>1$.

3. The constancy of the magnetizing function κ for very small forces, first observed by Lord Rayleigh, is confirmed. The boundary of proportionality between magnetizing forces and magnetic moments may be taken with sufficient accuracy for technical purposes as near the magnetizing force $H_1=0{\cdot}06$. This value represents a rather sudden transition in the curve $\kappa=f(H_1)$. Below this the deviations from proportionality are only very feeble, that is the curve $\kappa=f(H_1)$ passes into a parallel to the H-axis. The point at which it can be identified with a straight line (parallel) is different according to the nature of the iron investigated, and especially according to the sensitiveness of the apparatus used for the measurements, without varying much from a certain mean value which may be regarded as lying between the magnetizing forces $H_1=0{\cdot}03$ and $0{\cdot}04$.—Wiedemann's *Annalen*, No. 4, 1895.

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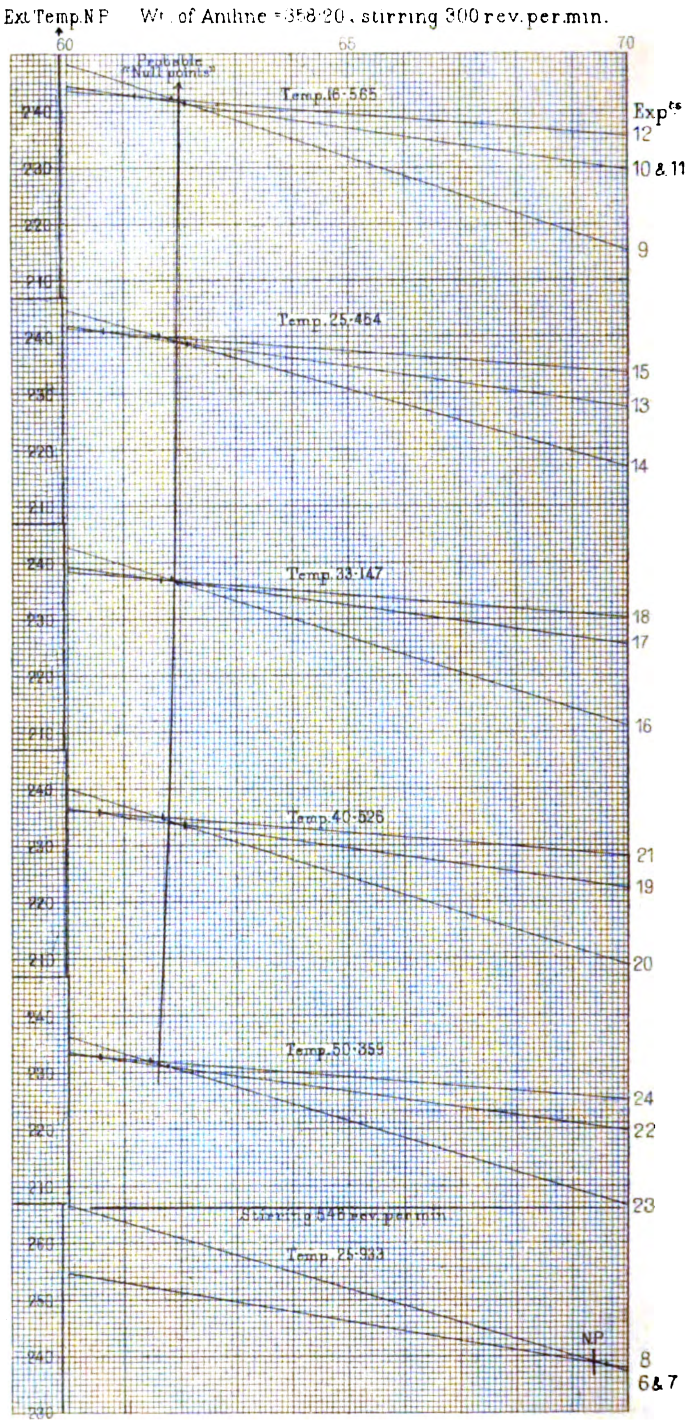

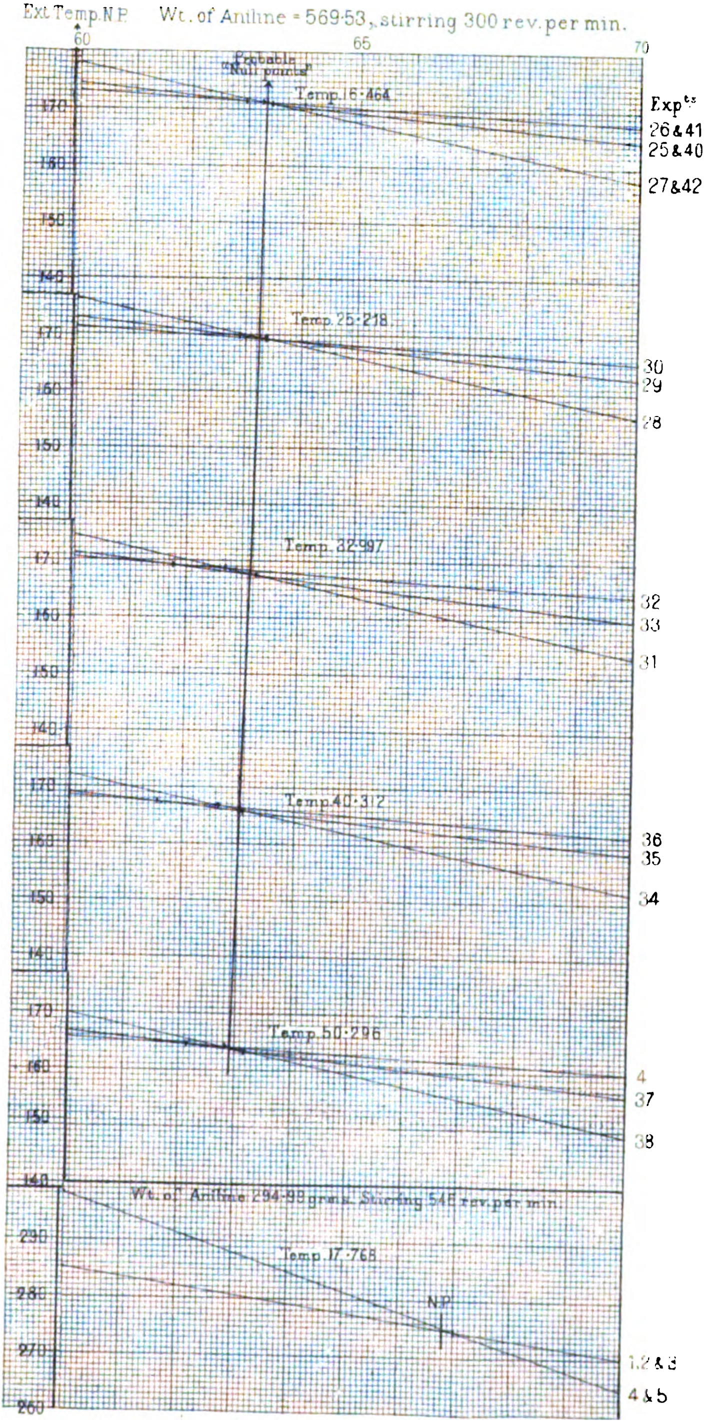

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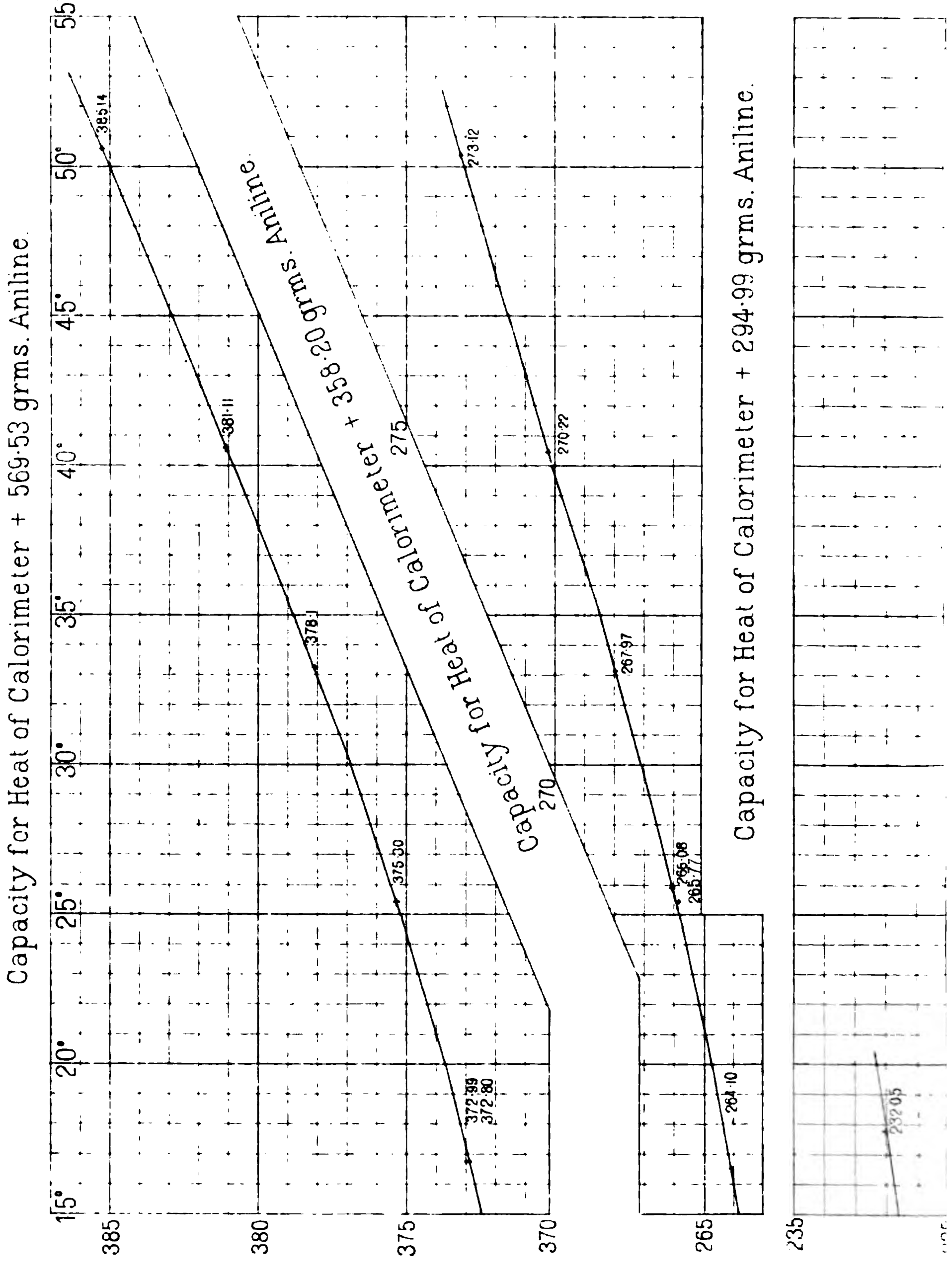
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385
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235
275
270
385·14
381·11
378·1
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264·10
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Chart B.

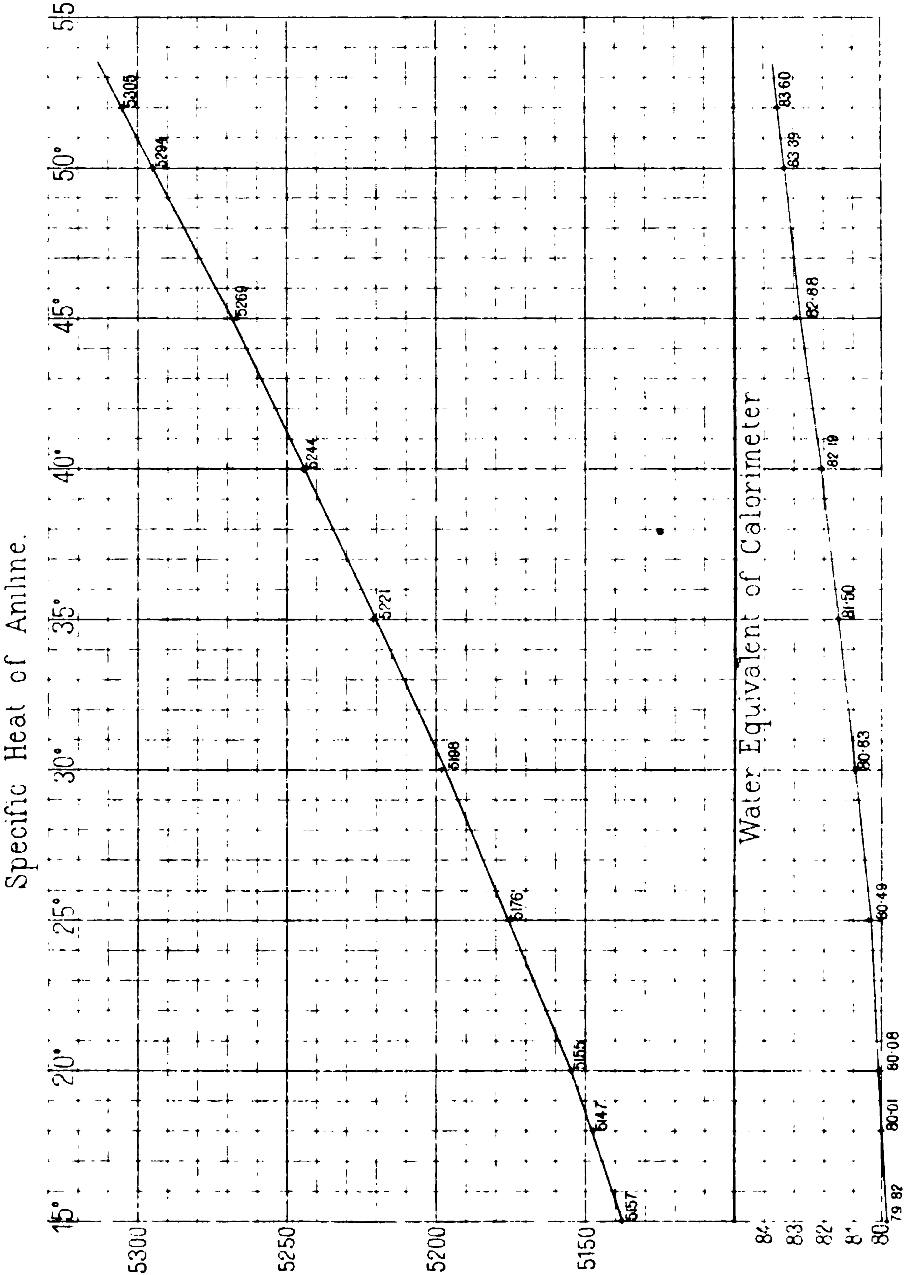

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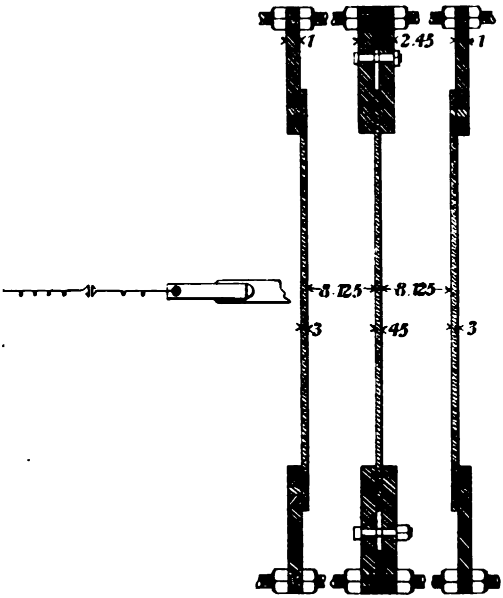
Fig. 3.



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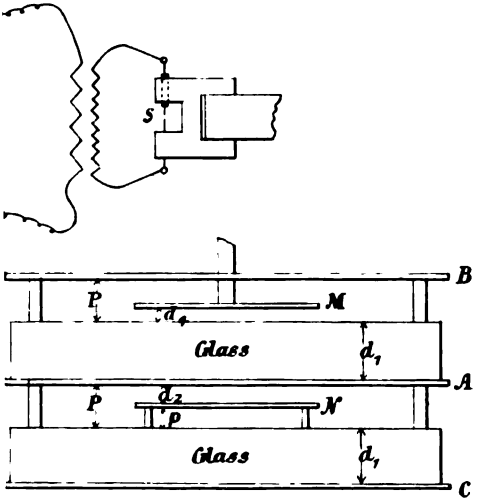

Fig. 4.

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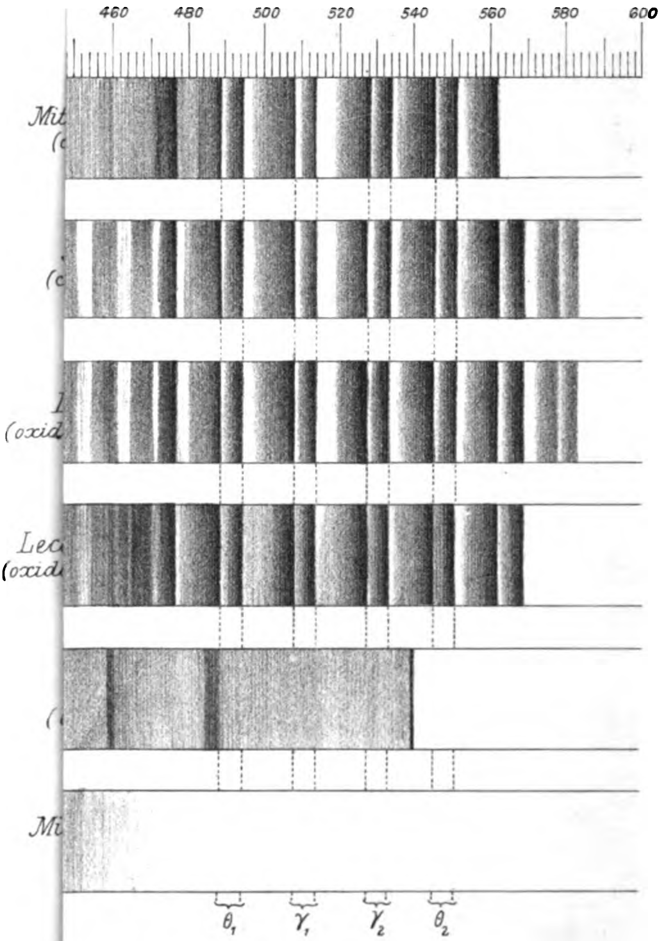

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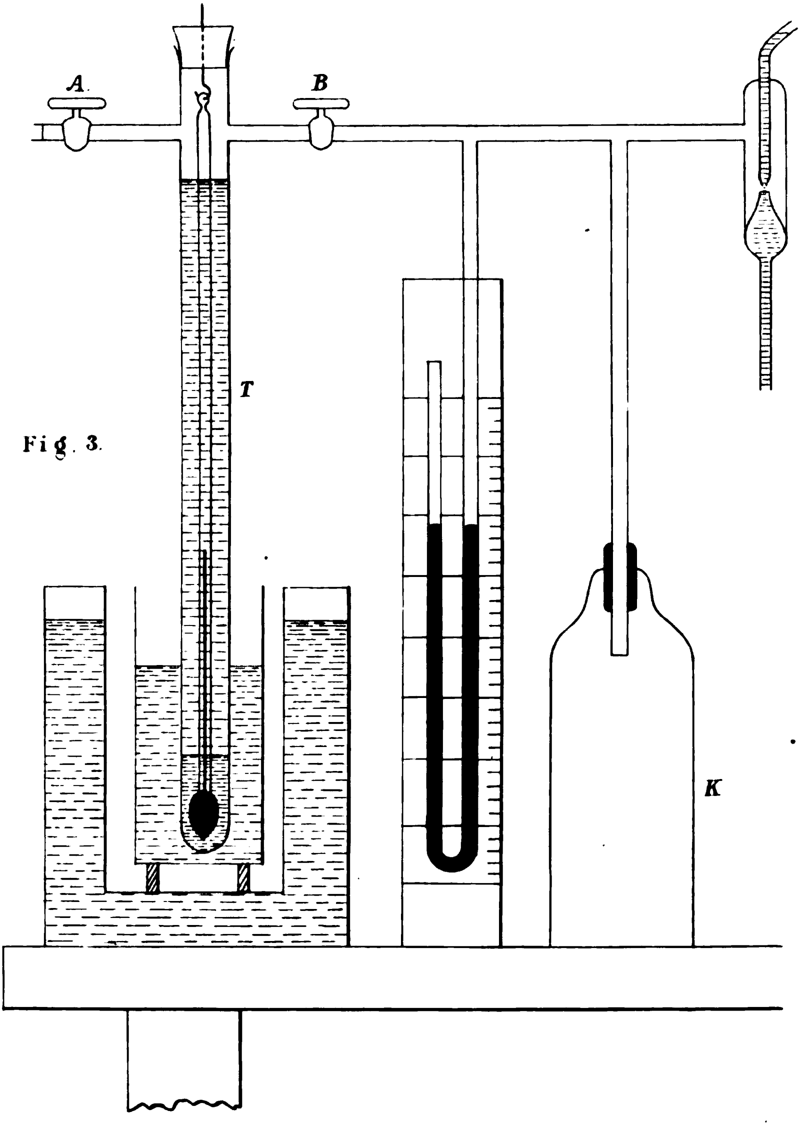
Fig. 3.



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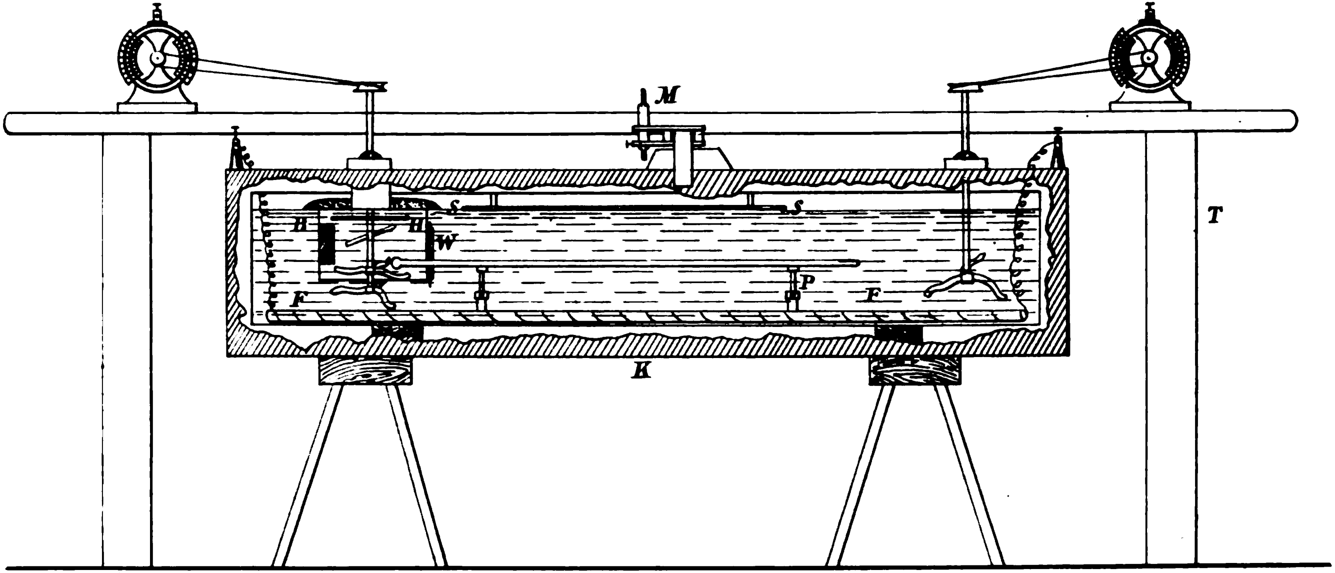

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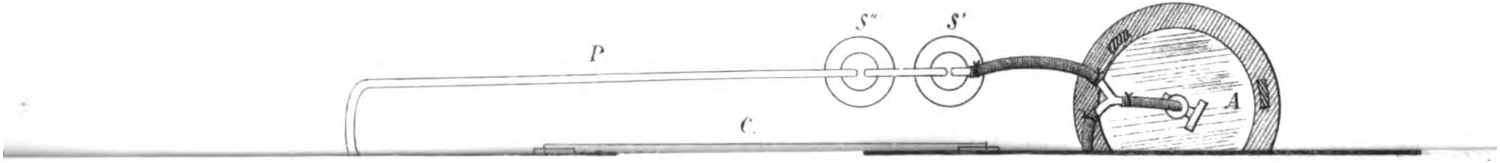

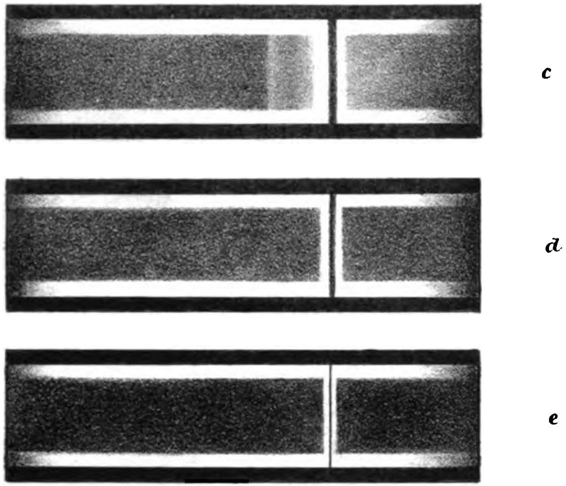

Fig. 3.

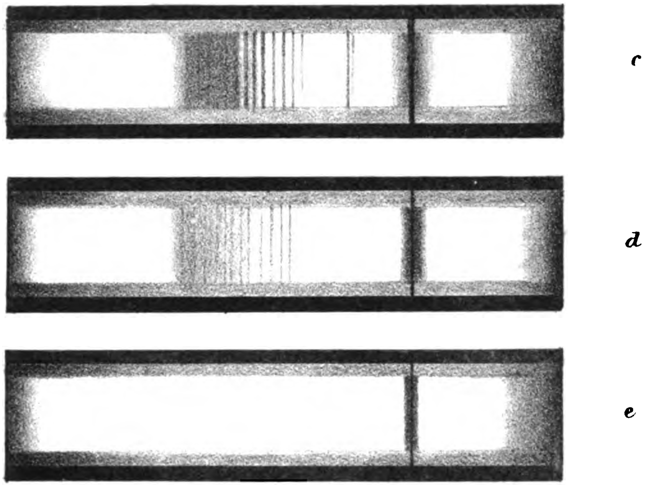

Fig. 4.

SPECTRA FROM HEATED SODIUM VAPOUR.

Note. — The continuous spectrum at the edges comes from the glowing walls of the tube.

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